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CONTROL TECHNIQUES FOR HYDROCARBON AND ORGANIC SOLVENT EMISSIONS FROM STATIONARY SOURCES

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U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Environmental Health Service

114

CONTROL TECHNIQUES FOR HYDROCARBON AND ORGANIC SOLVENT EMISSIONS FROM STATIONARY SOURCES

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Environmental Health Service
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PREFACE

Throughout the development of Federal air pollution legislation, the Congress has consistently found that the States and local governments have the primary responsibility for preventing and controlling air pollution at its source. Further, the Congress has consistently declared that it is the responsibility of the Federal government to provide technical and financial assistance to State and local governments so that they can undertake these responsibilities.

These principles were reiterated in the 1967 amendments to the Clean Air Act. A key element of that Act directs the Secretary of Health, Education, and Welfare to collect and make available information on all aspects of air pollution and its control. Under the Act, the issuance of control techniques information is a vital step in a program designed to assist the States in taking responsible technological, social, and political action to protect the public from the adverse effects of air pollution.

Briefly, the Act calls for the Secretary of Health, Education, and Welfare to define the broad atmospheric areas of the Nation in which climate, meteorology, and topography, all of which influence the capacity of air to dilute and disperse pollution, are generally homogeneous.

Further, the Act requires the Secretary to define those geographical regions in the country where air pollution is a problem—whether interstate or intrastate. These air quality control regions are designated on the basis of meteorological, social, and political factors which suggest that a group of communities should be treated as a unit for setting limitations on concentrations of atmospheric pollutants. Concurrently, the Secretary is required to issue air quality criteria for those pollutants he believes may be harmful to health or welfare, and to publish related information on the techniques which can be employed to control the sources of those pollutants.

Once these steps have been taken for any region, and for any pollutant or combination of pollutants, then the State or States responsible for the designated region are on notice to develop ambient air quality standards applicable to the region for the pollutants involved, and to develop plans of action for meeting the standards.

The Department of Health, Education, and Welfare will review, evaluate, and approve these standards and plans and, once they are approved, the States will be expected to take action to control pollution sources in the manner outlined in their plans.

At the direction of the Secretary, the National Air Pollution Control Administration has established appropriate programs to carry out the several Federal responsibilities specified in the legislation.

Control Techniques for Hydrocarbon and Organic Solvent Emissions from Stationary Sources is one of a series of documents to be produced under the program established to carry out the responsibility for developing and distributing control technology information. Previously, on February 11, 1969, control technique information was published for sulfur oxides and particulate matter.

In accordance with the Clean Air Act, a National Air Pollution Control Techniques Advisory Committee was established, having a membership broadly representative of industry, universities, and all levels of government. The committee, whose members are listed following this discussion, provided invaluable advice in identifying the best possible methods for controlling the pollution sources, assisted in determining the costs involved, and gave major assistance in drafting this document.

As further required by the Act, appropriate Federal departments and agencies, also listed on the following pages, were consulted prior to issuance of this document. A Federal consultation committee, comprising members designated by the heads of 17 departments and agencies, reviewed the document, and met with staff personnel of the National Air Pollution Control Administration to discuss its contents.

During 1967, at the initiation of the Secretary of Health, Education, and Welfare, several government-industry task groups were formed to explore mutual problems relating to air pollution control. One of these, a task group on control technology research and development, looked into ways that industry representatives could participate in the review of the control techniques reports. Accordingly, several industrial representatives, listed on the following pages, reviewed this document and provided helpful comments and suggestions. In addition, certain consultants to the National Air Pollution Control Administration also revised and assisted in preparing portions of this document. These also are listed on the following pages.

The Organic Solvents Advisory Committee also provided invaluable assistance by reviewing and commenting on the material in this document. Committee membership is indicated on the following pages.

The Administration is pleased to acknowledge efforts of each of the persons specifically named, as well as those of the many not so listed who contributed to the publication of this volume. In the last analysis, however, the National Air Pollution Control Administration is responsible for its content.

The control of air pollutant emissions is a complex problem because of the variety of sources and source characteristics. Technical factors frequently make necessary the use of different control procedures for different types of sources. Many techniques are still in the development stage, and prudent control strategy may call for the use of interim methods until these techniques are perfected. Thus, we can expect that we will continue to improve, refine, and periodically revise the control techniques information so that it will continue to reflect the most up-to-date knowledge available.

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TABLE OF CONTENTS

Section *Page*

LIST OF FIGURES xiv
LIST OF TABLES xv
SUMMARY xvii
1. INTRODUCTION 1-1
2. BACKGROUND INFORMATION 2-1
  2.1 DEFINITIONS 2-1
  2.2 PHOTOCHEMICAL REACTIONS 2-1
  2.3 STATIONARY SOURCES OF HYDROCARBON EMISSIONS 2-1
  2.4 REFERENCES FOR SECTION 2 2-2
3. CONTROL TECHNIQUES AND EQUIPMENT FOR STATIONARY SOURCES 3-1
  3.1 INTRODUCTION 3-1
  3.2 INCINERATION 3-1
    3.2.1 Basic Operating Principles and Equipment 3-2
      3.2.1.1 Direct Flame 3-2
      3.2.1.2 Catalytic Afterburners 3-3
      3.2.1.3 Process Heaters and Boilers 3-6
    3.2.2 Selection of an Afterburner 3-6
  3.3 ADSORPTION 3-7
    3.3.1 Introduction 3-7
    3.3.2 Basic Operating Principles 3-7
    3.3.3 Applications of Adsorption 3-8
      3.3.3.1 Types of Adsorbents 3-9
    3.3.4 Types of Adsorption Equipment 3-9
      3.3.4.1 Description of an Adsorption Process 3-9
      3.3.4.2 Factors Involved in Selection of an Adsorber . . . 3-12
    3.3.5 Instruments for Control of Adsorption Process 3-13
  3.4 ABSORPTION 3-14
    3.4.1 Introduction 3-14
    3.4.2 Applications 3-14
    3.4.3 Selection of an Absorbent 3-14
    3.4.4 Types of Absorbers 3-14
    3.4.5 Principles of Operation 3-16
  3.5 CONDENSATION 3-19
    3.5.1 Introduction 3-19
    3.5.2 Basic Operating Principles and Types of Equipment 3-21
    3.5.3 Design Factors and Applications 3-21
  3.6 USE OF LESS PHOTOCHEMICALLY REACTIVE MATERIALS . . . 3-23
    3.6.1 General Considerations 3-23
    3.6.2 Regulations Based on Photochemical Reactivity 3-24
    3.6.3 Rule 66 of Los Angeles County 3-24
    3.6.4 Background of Rule 66 3-24

Section *Page*

3.6.5 Applicability of Rule 66 to Other Areas 3-26
3.6.6 Regulation 3 of San Francisco Bay Area Air Pollution Control District 3-26
3.6.7 Photochemical Reactivity of Trichloroethylene 3-26
3.7 REFERENCES FOR SECTION 3 3-26
4. CONTROL SYSTEMS FOR INDUSTRIAL PROCESSES 4-1
4.1 PETROLEUM REFINERIES 4-1
4.1.1 Introduction 4-1
4.1.2 Storage 4-3
4.1.3 Waste-Gas Disposal Systems 4-4
4.1.3.1 Pressure-Relief Systems 4-4
4.1.3.2 Flares 4-5
4.1.4 Oil-Water Effluent Systems 4-5
4.1.5 Cracking Catalyst Regeneration 4-6
4.1.6 Pumps 4-6
4.1.7 Airblowing of Asphalt 4-7
4.1.8 Valves 4-8
4.1.9 Loading Facilities 4-8
4.1.10 Vacuum Jets 4-8
4.1.11 Boilers and Process Heaters 4-8
4.1.12 Chemical Treating Processes 4-8
4.2 GASOLINE DISTRIBUTION SYSTEMS 4-8
4.2.1 Introduction 4-8
4.2.2 Emissions 4-9
4.2.3 Controls 4-10
4.2.3.1 Overhead Loading 4-10
4.2.3.2 Bottom Loading 4-11
4.2.3.3 Vapor Disposal 4-12
4.2.4 Regulations and Costs 4-13
4.3 CHEMICAL PLANTS 4-13
4.3.1 Introduction 4-13
4.3.2 Processes 4-14
4.3.3 Emission Control 4-16
4.3.3.1 Collection of Vented Gases 4-17
4.3.3.2 Halogenation 4-17
4.3.3.3 Disposal of Waste Gases 4-18
4.4 PAINT, LACQUER, AND VARNISH MANUFACTURE 4-18
4.4.1 Introduction 4-18
4.4.2 Paint Manufacturing 4-18
4.4.3 Lacquer Manufacturing 4-20
4.4.4 Varnish Manufacturing 4-21
4.4.4.1 Introduction 4-21
4.4.4.2 Manufacturing Processes and Emissions 4-21
4.4.4.3 Controls 4-23
4.5 RUBBER AND PLASTIC PRODUCTS MANUFACTURE 4-25
4.5.1 Introduction 4-25
4.5.2 Rubber Manufacture 4-25

Section *Page*

4.6 SURFACE COATING APPLICATIONS 4-26
    4.6.1 Introduction 4-26
    4.6.2 Emissions 4-27
    4.6.3 Control Techniques and Costs 4-27
4.7 DEGREASING OPERATIONS 4-28
    4.7.1 Introduction 4-28
    4.7.2 Vapor Degreasing Equipment 4-30
4.8 DRY CLEANING 4-31
    4.8.1 Introduction 4-31
    4.8.2 Process Description 4-31
    4.8.3 Solvent Emissions 4-32
    4.8.4 Control Techniques and Costs 4-32
4.9 STATIONARY FUEL COMBUSTION 4-33
    4.9.1 Introduction 4-33
    4.9.2 Processes and Emissions 4-33
    4.9.3 Control Techniques 4-33
        4.9.3.1 Operating Practices 4-33
        4.9.3.2 Improved Equipment Design 4-34
        4.9.3.3 Fuel Substitution 4-34
    4.9.4 Control Costs 4-34
4.10 METALLURGICAL COKE PLANTS 4-34
    4.10.1 Process Descriptions 4-34
    4.10.2 Emissions 4-35
    4.10.3 Control of Emissions 4-35
4.11 SEWAGE TREATMENT 4-37
    4.11.1 Introduction 4-37
    4.11.2 Process Description and Emissions 4-37
    4.11.3 Control Techniques and Costs 4-37
4.12 WASTE INCINERATION AND OTHER BURNING 4-38
    4.12.1 Introduction 4-38
    4.12.2 Emissions 4-38
    4.12.3 Controls 4-42
        4.12.3.1 Waste Disposal 4-42
        4.12.3.2 Incineration 4-42
        4.12.3.3 Forest Wildfires 4-43
        4.12.3.4 Controlled Vegetation Burning 4-44
        4.12.3.5 Coal Refuse Fires 4-44
        4.12.3.6 Structural Fires 4-44
    4.12.4 Costs 4-44
4.13 MISCELLANEOUS 4-45
    4.13.1 Introduction 4-45
    4.13.2 Fermentation Processes 4-45
    4.13.3 Food Processing 4-45
    4.13.4 Charcoal Manufacture 4-46
    4.13.5 Drug Manufacture 4-46
4.14 REFERENCES FOR SECTION 4 4-46

Section *Page*

5. EMISSION FACTORS 5-1
   5.1 REFERENCES FOR SECTION 5 5-3
6. ECONOMICS 6-1
   6.1 INTRODUCTION 6-1
   6.2 DEFINITION OF ALTERNATIVES 6-1
   6.3 IDENTIFICATION OF COSTS 6-1
      6.3.1 Capital Investment 6-2
      6.3.2 Maintenance and Operation 6-2
      6.3.3 Annualized Costs 6-2
   6.4 COST CURVES BY EQUIPMENT TYPES 6-3
      6.4.1 Afterburners 6-3
      6.4.2 Activated-Carbon Adsorbers 6-3
      6.4.3 Absorption Equipment 6-4
      6.4.4 Condensers 6-5
   6.5 VALUE OF RECOVERED MATERIALS 6-5
   6.6 REFERENCES FOR SECTION 6 6-6
7. CURRENT RESEARCH 7-1
   7.1 RESEARCH PROJECTS APPLICABLE TO HYDROCARBONS AND ORGANICS 7-1
   7.2 RESEARCH ON CONTROL EQUIPMENT AND TECHNIQUES . . . 7-1
   7.3 CURRENT RESEARCH PROJECTS 7-2
   7.4 REFERENCES FOR SECTION 7 7-3
8. SUBJECT INDEX I-1

LIST OF FIGURES

Figure

3–1. Typical Multijet Burner Arrangement Used in Direct-Flame Afterburner 3-3
3–2. Direct-Flame Afterburner, Vertical Arrangement 3-4
3–3. Raw Gas Burner and Multiple Jet Grid 3-4
3–4. Afterburner With Heat Exchanger 3-5
3–5. Catalytic Afterburner 3-6
3–6. Diagrammatic Sketch of Two-Unit Fixed-Bed Adsorber 3-11
3–7. Diagrammatic Sketch of Vertical Adsorber with Two Cones, Permitting Studies on Different Depths of Carbon Beds 3-11
3–8. Standard Skid-Mounted Vapor-Recovery Unit 3-12
3–9. Schematic Diagram of a Bubble-Cap Tray Tower 3-15
3–10. Packed Tower 3-15
3–11. Spray Tower 3-15
3–12. Venturi Scrubber 3-16
3–13. Driving Force for Absorption 3-16
3–14. Common Tower Packing Materials 3-17
3–15. Number of Transfer Units for Absorbers or Strippers With Constant Absorption Stripping Factor 3-17
3–16. Types of Condensers 3-22

Figure *Page*
4–1. Processing Plan for Typical Complete Refinery 4-2
4–2. Representation of Gasoline Distribution System 4-9
4–3. View of Bottom-Loading Station 4-10
4–4. View of Mobil Oil Corporation Vapor Closure 4-11
4–5. Chiksan Pneumatically Operated Loading Assembly With Integrated Vapor Closure and Return Line 4-11
4–6. View of Greenwood Vapor Closure 4-12
4–7. SOCO Vapor Closure Device in Filling Position 4-12
4–8. Small Capacity Vaporsaver Gasoline Absorption Unit 4-13
4–9. Automatic Jet Compressor 4-17
4–10. Direct-Fired Afterburner for Control of Emissions from Two Phthalic Anhydride Production Units 4-19
4–11. Schematic Plan for Varnish-Cooking Control System 4-25
4–12. Self-Recuperating Heat Recovery: Single Efficiency Heat Exchange 4-29
4–13. Self-Recuperating Heat Recovery: Variable Heat Exchange 4-29
4–14. Self-Recuperating Heat Recovery: Variable Efficiency Heat Exchange . 4-29
4–15. Domestic Gas-Fired Incinerator 4-39
4–16. Single-Chamber Incinerator 4-39
4–17. Cutaway of an In-Line Multiple-Chamber Incinerator 4-40
4–18. Section of the Flue-Fed Incinerator 4-40
4–19. Section of Chute-Fed Apartment Incinerator 4-40
4–20. Section of Pathological Incinerator 4-41
4–21. Section of Municipal Incinerator 4-41
4–22. Land Waste-Disposal Costs 4-45
4–23. Cost of Incinerator at Three Levels of Control of Particulate Emissions 4-45
6–1. Purchase Cost of Afterburners, 1968 6-3
6–2. Adsorption System Installed Costs, 1969 Basis 6-4
6–3. Packed Tower Costs, with Raschig Rings as Packing, 1969 Basis 6-4
6–4. Purchase Costs of Condensers 6-5

LIST OF TABLES

Table
2–1. Summary of Nationwide Hydrocarbon Emissions, 1968 2-2
3–1. Gases and Vapors Selectively Adsorbed By Activated Carbon 3-10
3–2. Constants For Use in Determining Gas-Phase Height of Transfer Units 3-18
3–3. Constants for Use in Determining Liquid-Phase Height of Transfer Units 3-19
3–4. Pressure Drop Constants for Tower Packing 3-20
3–5. Representative Applications of Condensers in Air Pollution Control 3-23
4–1. Typical Analysis of Vapors From Loading of Gasoline into Tank Trucks 4-9

Table *Page*

4–2. Quantities of Raw Materials and Intermediate Products Converted to Synthetic Organic Chemicals in 1967 4-14

4–3. Calculation of Hydrocarbon Losses From Process Equipment 500-Million-lb/yr Ethylene Plant 4-16

4–4. Average Hydrocarbon Emissions From Stationary Fuel Combustion Sources 4-33

4–5. Trends in Overall Efficiency of Steam-Electric Generating Plants 4-34

4–6. Typical Composition and Amounts of Compounds Removed Per Ton of Coal 4-36

4–7. Organic Vapor Concentrations Emitted From An Activated Sludge Plant 4-37

4–8. Estimated National Emissions From Incineration and Other Burning 4-42

5–1. Emission Factors for Hydrocarbons 5-1

SUMMARY

The effects of hydrocarbon and organic solvent emissions are of two types, direct and indirect. Direct effects are caused by the original, unaltered emissions, and indirect effects are caused by substances formed by photochemical reactions of the original emissions with other substances in the atmosphere. The purpose of this document is to make information available on techniques for the control of organic emissions from stationary sources.

STATIONARY SOURCES OF HYDROCARBON AND ORGANIC SOLVENT EMISSIONS

Sources of hydrocarbon emissions include petroleum refining, gasoline distribution and marketing, chemical manufacturing, coal coking, fuel burning, waste disposal, and food processing. Sources of organic solvent emissions include manufacture and application of protective coatings, manufacture of rubber and plastic products, degreasing and cleaning of metal parts, dry cleaning operations, printing, and manufacture of chemicals.

CONTROL TECHNIQUES AND EQUIPMENT

Methods used to control hydrocarbon and organic solvent emissions are (1) operational or process changes, (2) substitution of materials, and (3) installation of control equipment. The techniques used in control devices are of four classifications: incineration, adsorption, absorption, and condensation.

Incineration devices are of two types, direct-flame afterburners and catalytic afterburners. Direct-flame afterburners utilize a flame to complete oxidation of the organic emissions. Flame coverage, turbulence, effluent residence time, and temperature are important in the design of an afterburner. Temperatures of 1200° to 1400°F and residence times of 0.3 to 0.6 second are usually required. Removal efficiencies of direct-flame afterburners can be high; organic particulates are removed effectively; and no secondary disposal problems are encountered. Operational costs are high unless heat-recovery equipment is installed.

Catalytic afterburners utilize a catalyst so that emissions can be oxidized at a lower temperature than could otherwise be done. Fuel costs are thus lower, but removal efficiencies are also lower. Catalysts are subject to poisoning and deactivation from the heat present.

Activated-carbon adsorbers collect organic vapors in the capillary surface of the solid adsorbent. After the carbon bed has adsorbed the optimum amount of organic material, the gas stream is stopped and the carbon bed is steam stripped to remove the organic material. The carbon bed is then ready for reuse. The steam and organic material are condensed, and the organic is recovered by decantation or distillation. Two or more carbon-containing vessels are used, one adsorbing while the other is desorbing.

Costs of adsorbing systems and their operations are high, but recovery of valuable materials enhances the feasibility of such operations. High removal efficiencies are possible. Streams containing resin-forming gases cannot be handled by carbon adsorbers because the resins plug the carbon beds.

Absorption is the transfer of a soluble component of a gas phase into a relatively nonvolatile liquid absorbent. Common absorbents are water, mineral oil, nonvolatile hydrocarbons, and aqueous solutions such as solutions of oxidizing agents or alkalis. Contact between gas and liquid is provided in bubble-plate columns, packed towers, jet scrubbers, spray towers, and venturi scrubbers.

Absorbers are widely used when gas and vapor concentrations are high; however, such equipment is usually classified as production equipment, and not as emission control equipment. Absorbers are not widely used when concentrations are low since large and expensive equipment would be required to achieve good removal efficiencies.

Condensers collect organic emissions by lowering the temperature of the gaseous stream to the condensation point of that material. Condensers are of two types, contact and surface. In contact condensers, the gaseous stream is brought into direct contact with the cooling liquid, the condensed material mixing with the coolant. In a surface condenser, the vapor to be condensed and the cooling fluid are separated by a metal wall.

Condensers used in the petroleum and chemical industries to condense concentrated vapors are classified as production equipment. High removal efficiency cannot be achieved with low concentrations; condensers are, therefore, useful as preliminary devices to be followed by a more efficient device such as an afterburner or adsorber.

Use of Less Photochemically Reactive Materials

Collection of organic emissions from the painting of buildings and structures is impractical. In operations wherever collection is possible but is not financially feasible, substitution of less reactive materials is a possible control technique.

Los Angeles County limits the emissions from organic solvents by Rule 66. All the normally used solvents are divided into two groups, those classified as photochemically reactive and those not photochemically reactive. Emissions from the reactive group are restricted, but emissions from the nonreactive group are not limited, except when flame contact, baking, or heat-curing is involved. Many solvents with more than the allowed amount of reactive materials have been reformulated by the manufacturer with materials in the nonreactive group.

The San Francisco Bay Area Air Pollution Control District limits emission of only very reactive compounds. These are defined as olefins, substituted aromatics, and aldehydes.

Control Systems for Industrial Processes

Petroleum Refining

Evaporation losses during storage are minimized by use of floating roof tanks, pressure tanks, and vapor conservation or recovery systems. Hydrocarbons from catalyst regenerators can be controlled by waste heat boilers. Leakage from valves, pumps, and compressors can be reduced by systematic maintenance of connections and seals. Waste water separators can be controlled by enclosing the separator tanks. Vapor recovery systems or smokeless flares are utilized to control hydrocarbon vapors from blowdown systems. Stripping gases from acid treating, doctor treating, and caustic treating and air-blowing effluents can be controlled by incineration.

Gasoline Distribution Systems

Vapors emitted during the loading of gasoline tank trucks can be collected and delivered to a vapor disposal system. The collection system consists of a tight fitting hatch and a vapor delivery line. For top-loading tanks, the vapor delivery line is an annular space around the gasoline delivery line. For bottom-loading tanks, the vapor line is a separate line connected at the top of the tank. Vapors can be delivered to a gas-blanketed vapor holder and used as fuel in boilers and heaters where the load rack is adjacent to the refinery. For storage and loading facilities at other locations, packaged vapor recovery units have been developed in which the vapors are compressed and reabsorbed in gasoline.

Chemical Plants

The principal raw materials for synthetic organic products are derived mostly from petroleum and to a lesser extent from the by-products of the coking of coal. These materials are processed through the following types of conversions: alkylation, hydrogenation, dehydrogenation, dehydration, esterification, halogenation and dehalogenation, oxidation, nitration, and polymerization.

Waste gases from processing units can be collected and delivered to a burner, to a gas holder, or into a fuel header system. Waste gases from units producing chlorinated hydrocarbons can be processed to recover by-product hydrochloric acid. Direct flame and catalytic afterburners are used to eliminate organic vapors and mists from many off-gases.

Paint, Lacquer, and Varnish Manufacture

Emissions from paint and lacquer manufacture occur during mixing, grinding, and thinning operations. Varnish ingredients must be "cooked" to promote such reactions as depolymerization, esterification, isomerization, melting, and bodying. Emissions contain fatty acids, aldehydes, acrolein, glycerol, acetic acid, formic acid, and complex residues of thermal decomposition. Control systems consist of condensers, scrubbers, and afterburners.

Rubber and Plastic Products Manufacture

Emissions from rubber product manufacture occur during heat plasticization, chemical plasticization, and vulcanization. Control techniques include carbon adsorption, direct-flame and catalytic incineration, and reformulation to nonphotochemically reactive materials. In plastic products manufacture, emissions can occur from curing ovens, particularly when dioctyl phthalate is used as a plasticizer. Such mists can be controlled with high-energy scrubbers or with afterburners.

Surface Coating Applications

Emissions of hydrocarbons from the application of paint, varnish, and similar coatings are due to the evaporation of the solvents, diluents, and thinners. Where controls are required, reformulation with nonphotochemically reactive solvents is a method of control. Afterburners have been used to control emissions from paint bake ovens. These ovens can sometimes be redesigned to reduce the volume of gases to be handled, effecting considerable savings. Heat recovery systems can lower operating costs by reducing fuel requirements.

Degreasing Operations

Most vapor-phase degreasers use chlorinated hydrocarbon solvents, principally trichloroethylene. Less photochemically reactive 1,1,1-trichloroethane (methyl chloroform) and perchloroethylene can be substituted. Activated-carbon adsorbers can be used to control emissions in some applications. Solvent emissions can be minimized by elimination of drafts, good drainage of work items, controlled speed of work entering and leaving work zone, and covering of tank whenever possible.

Dry Cleaning

Dry cleaning is done by two processes: those using petroleum solvents and those using perchloroethylene or other halogenated solvents. In plants using perchloroethylene, vapor is recovered by water-cooled condensers, which may be followed by activated-carbon adsorbers. The value of the solvent makes recovery economically feasible. Plants using petroleum solvents can be controlled, if necessary, by using solvents reformulated to be nonphotochemically reactive. Control by activated carbon may be feasible.

Stationary Fuel Combustion

Hydrocarbons may be emitted if combustion is not complete. When properly designed and operated, stationary fuel combustion equipment is not a serious source of organic emissions.

Metallurgical Coke Plants

The hydrocarbons from the coking of coal are collected to recover by-products. Emissions occur during charging operations and from improperly fitting doors and other leaks. Emissions during charging can be reduced by steam-jet aspirators in the collection pipes. Self-sealing doors and good maintenance programs can reduce emissions.

Sewage Treatment Plants

Primary sewage plants emit hydrocarbons from the screening and grit chambers, and from the settling tanks. Activated-sludge plants emit gas from the aeration tanks. Trickling filter plants emit organic gas from the filters, the clarifiers, and from the sludge-digestion tanks. Control of emissions can be accomplished by covering or enclosing the various treating units and oxidizing or combusting the effluent gases.

Waste Disposal

Burning of waste materials can cause emissions of hydrocarbons. Open burning and inefficient incinerators are the predominant sources of such emissions. Control can be achieved by the use of multiple-chamber incinerators or by disposing of the waste in sanitary landfills.

Miscellaneous Operations

Emissions from deep fat fryers and coffee roasters can be controlled by afterburners. Fish cookers can be controlled by condensers. Evaporators of liquids from fish processing can be controlled by condensers and scrubbers, and fish meal driers by scrubbing with chlorinated water. Noncondensible gases from charcoal manufacturing can be burned.

ECONOMICS

Economic considerations in air pollution control include: (1) the selection of control techniques and equipment; (2) the assessment of the impact of control on product prices, profits, investments, and value added to the product; and (3) the identification of the many direct and indirect costs of installing and operating air pollution control equipment. Process alterations or substitutions are usually considered first in selecting a control technique. If control equipment is necessary, the required emission reduction, process stream characteristics, and plant facilities are evaluated in order to select the system that will optimize costs and benefits. Value of recovered materials may be a significant cost offset.

CONTROL TECHNIQUES FOR HYDROCARBON AND ORGANIC SOLVENT EMISSIONS FROM STATIONARY SOURCES

1. INTRODUCTION

Pursuant to authority delegated to the Commissioner of the National Air Pollution Control Administration, *Control Techniques for Hydrocarbon and Organic Solvent Emissions From Stationary Sources* is issued in accordance with Section 107(c) of the Clean Air Act as amended (42 U.S.C. 1857-18571).

This document has been prepared to summarize current information on stationary sources of hydrocarbons and organic solvent emissions, methods of control, and the costs and cost-effectiveness of controls.

The available control techniques for these emissions vary in type, application, effectiveness, and cost. By far the most important technique for controlling air pollution is in the basic design of equipment to utilize efficiently or consume completely the processed materials. Failing this, control equipment can be used to reduce emissions. Operating principles, design characteristics, advantages, disadvantages, applications, and costs of the various control equipment and techniques are described herein.

The control techniques described in this document represent a broad spectrum of information from many technical fields. The devices, methods, and principles have been developed and used over many years and are constantly being revised and improved. They are recommended as the techniques generally available to control hydrocarbon and organic solvent emissions.

The many industrial processes involved are described individually in this document. The various techniques and control systems that can be applied to remove the pollutants from these processes are reviewed and compared. Sections are included on emission factors, equipment costs and cost-effectiveness analysis, and current research and development.

The proper choice of a method, or combination of methods, to control emissions from a specific source depends on many factors other than the source characteristics alone. For this reason, no attempt is made here to review all possible combinations of control techniques that may be required to completely remove a certain emission.

In some applications, it would be unwise to attempt to control organic vapors by a method that may be the preferred one for other organics. For example, if combustion is used to control organic vapors that contain halogens, sulfur, or nitrogen, the combustion products may be less desirable and more corrosive than the original emission. Another type of control system such as a scrubber may then be required in series with the burner to remove the harmful components from these combustion products.

Mobile sources of hydrocarbon and organic emissions are described in AP-66, *Control Techniques for Carbon Monoxide, Nitrogen Oxide, and Hydrocarbon Emissions from Mobile Sources,* which is being published simultaneously with this and other documents on control techniques for air pollutant emissions.

While some data are presented on quantities of hydrocarbons and organic solvents emitted to the atmosphere, the effects upon health and welfare of hydrocarbons and secondary atmospheric reaction products are considered in two companion documents, AP-64, *Air Quality Criteria for Hydrocarbons* and AP-63, *Air Quality Criteria for Photochemical Oxidants.*

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2. BACKGROUND INFORMATION

2.1 DEFINITIONS

Hydrocarbons contain only the elements hydrogen and carbon. Organic solvents may contain, in addition to hydrogen and carbon, one or more of the following elements: oxygen, nitrogen, sulfur, and halogens. In this document the term "organic solvents" is intended to include such other materials as diluents and thinners.

A discussion of the nomenclature of organic compounds is beyond the scope of this work; the reader may find information of this nature in a reference book.[1] A definition of generic names of some of the more important compounds and types of compounds is pertinent, however.

The major divisions of hydrocarbons are (1) aromatic, (2) aliphatic, and (3) alicyclic. If within the structure of the molecule there is a benzene structure (⌬ , a six-carbon ring containing three double bonds), the hydrocarbon is aromatic. If no ring structure exists, the compound is said to be aliphatic. If a ring structure other than the benzene ring is present, the compound is said to be alicylic. Many further subdivisions exist within these divisions.

Aliphatic hydrocarbons include both saturated paraffinic compounds (C_nH_{2n+2}) and unsaturated compounds. Unsaturated compounds are compounds with carbon-carbon double (alkenes) or triple (alkynes) bonds. Alkenes are perhaps better known as olefins and have the type formula C_nH_{2n}. Olefins are generally regarded as being the most reactive of the organic compounds in photochemical smog formation, although reactivity varies widely with chemical structure.

2.2 PHOTOCHEMICAL REACTIONS

Gaseous organic compounds in the atmosphere may undergo chemical and physical processes that produce other substances with greatly altered properties. These reactions are photochemical in nature. A description of these processes and the effects of the products are given in AP-63, *Air Quality Criteria for Photochemical Oxidants,* U.S. Department of Health, Education, and Welfare, National Air Pollution Administration, and in AP-64, *Air Quality Criteria for Hydrocarbons,* U.S. Department of Health, Education, and Welfare, National Air Pollution Control Administration.

2.3 STATIONARY SOURCES OF HYDROCARBON EMISSIONS

Atmospheric hydrocarbons and other organic compounds can be thought of as having four origins: petroleum, coal, natural gas, and biological products. Organic gases can escape to the atmosphere at many points during the production, processing, storage, transport, and ultimate use of the originating organic material.

Potential sources of hydrocarbon emissions in petroleum production and product processing include leakage from oil field operations, refining, gasoline storage tanks, gasoline loading facilities, blowing of asphalt, blowdown systems, catalyst regenerators, processing vessels, flares, compressors, pumps, vacuum jets, waste-effluent handling equipment, and turnaround operations.

Gasoline distribution and marketing systems emit hydrocarbon vapors from tank-truck loading racks, service station tank-filling operations, and automobile tank-filling operations.

Organic solvents are derived mainly but not exclusively from petroleum. They are used in many kinds of operations. Chemical, drug, and pharmaceutical manufacturing plants car be sources of organic emissions from those operations involving the use of organic solvents. Rubber and plastic product manufacturing often involves the use of organic-solvent-based-adhesives and other solvent uses that lead to organic emissions. Paint and varnishes, lacquers, under-coatings, etc., are composed of 40 to 80 percent organic solvents, which evaporate during or after the application of the coating. Degreasing and cleaning of metal items can cause significant organic emissions. Vapor-phase degreasing is the most widely used method, but spray degreasing is also used. Drycleaning of clothing utilizes organic solvents and contributes to emissions. The manufacturing processes for solvents and solvates are also potential sources.

Metallurgical coke plants emit varying amounts of hydrocarbons, depending on type of furnace, operating methods, maintenance practices, and other factors.

Fuel-burning equipment of all types can emit organics if it is not properly adjusted, not adequately maintained, or not operated correctly.

Waste disposal by burning can cause organic emissions from incomplete combustion. Open burning of refuse is the greatest offender in this category. Inefficient incinerators are also significant sources. Carbonaceous material from many sources is disposed of by burning.

Miscellaneous sources of organic gases from biological sources include fermentation processes, food processing, organic fertilizer processing, wood distillation, and soap manufacturing.

Estimates for total United States organic emissions from stationary sources are presented in Table 2-1. These estimates in general were made from emission factors and quantities of fuels consumed, quantities of refuse burned, and quantities of raw materials processed. Although they represent only gross approximations, they are the best estimates currently available.

Table 2-1. SUMMARY OF NATIONWIDE HYDROCARBON EMISSIONS, 1968[2]

(10^6 tons/year)

Source	Emissions
Transportation	
Motor vehicles	
Gasoline	15.2
Diesel	0.4
Aircraft	0.3
Railroads	0.3
Vessels	0.1
Nonhighway use, motor fuels	0.3
Fuel combustion–stationary	
Coal	0.2
Fuel oil	0.1
Natural gas	Negligible
Wood	0.4
Industrial processes	4.6
Solid waste disposal	1.6
Miscellaneous	
Forest fires	2.2
Structural fires	0.1
Coal refuse	0.2
Agricultural burning	1.6
Organic solvent evaporation[a]	3.2
Gasoline marketing	1.2
Total	32.0

[a] Includes estimated 25 percent aldehydes, ketones, and esters, and 10 percent chlorinated solvents.

2.4 REFERENCES FOR SECTION 2

1. Introduction, with Key and Discussion of the Naming of Chemical Compounds for Indexing. Chem. Abstracts Subject Index. *56:* 1N-98N, Jan-June, 1962.
2. National Air Pollution Control Administration, Reference Book of Nationwide Emissions. U.S. DHEW, PHS, CPEHS, NAPCA. Durham, N.C.

3. CONTROL TECHNIQUES AND EQUIPMENT FOR STATIONARY SOURCES

3.1 INTRODUCTION

Methods now employed commercially to control the emission of organic air pollutants are (1) operational or process changes, (2) substitution of a higher-boiling- point material and/or a less reactive compound in the process, and (3) installation of control equipment to capture of destroy the organic vapors emitted from the process. By far the most important technique for controlling air pollution is to design basic equipment for utilizing efficiently or consuming completely the materials being processed. Failing this, control equipment must be used in order to reduce organic emissions. Commercially available control techniques may be divided into five general classifications: incineration, adsorption, absorption, condensation, and substitution of other materials. These techniques are discussed in this chapter. Basic operating principles of equipment employed are explained, and their areas of application are indicated. The significant factors affecting their operation are outlined, and general cost information is provided.

3.2 INCINERATION

Incineration is the control of organic emissions by combustion. The objective is to oxidize completely the organic vapors and gases from a process or operation that emits them. Some emissions, of course, include particulate as well as gaseous matter. If the particulates are combustible, they may also be handled by the combustion process. Incineration devices have been widely and successfully used for reducing organic emissions. They offer the potential of heat recovery.

Devices in which dilute concentrations of organic vapors are burned by the use of added fuel are known as afterburners. Devices used to burn waste gases having sufficient heating value to burn without added fuel are known as flares if there is no air premixing or as incinerators if there is air premixing. Flares are discussed in Section 4.1, Petroleum Refineries.

Afterburners are gas-cleaning devices that incinerate organic emissions. Combustion is accomplished either by direct-flame incineration or by catalytic oxidation. Under the proper conditions, the firebox of a process heater or boiler may also be used as an afterburner.

In practice, it would usually be unwise to attempt to control, solely by combustion, organic vapors that contain halogens or sulfur, since the combustion products of such materials are usually less desirable and often corrosive. A secondary control system such as a scrubber may be required in series with the afterburner to remove these contaminants.

Industrial processes for which control by afterburners is satisfactory include solvent operations, drying, baking, and curing operations performed in ovens, dryers, and kilns. Successful combustion control devices have been applied to aluminum chip dryers, petroleum processing, animal blood dryers, automotive brakeshoe debonding ovens, citrus pulp dryers, coffee roasters, wire enameling ovens, incinerators, foundry core ovens, meat smokehouses, paint-baking ovens, varnish cookers, paper printing and impregnating, pharmaceutical manufacturing, sewage disposal, chemical processing, and textile finishing. In many of these operations, the afterburners reduce the amount of particulate matter as well as the organic vapors present in the gas stream, and thereby reduce the opacity of the exhaust gas.

3.2.1 Basic Operating Principles and Equipment

3.2.1.1 Direct Flame

For combustion of organic vapors and liquids, the concentrations of vapor and air must be within the limits of flammability. These limits are the mixture ratios of vapor and air that are either too rich or too lean to ignite. These limits exist because flammation proceeds by accumulation of thermal energy. Their value for different mixtures will be determined by the heat of reaction, the thermal conductivities, rates of diffusion, and specific heats of the components.

In order that a flame be self-sustaining, the mixture of air and combustibles must provide enough heat to maintain the combustion temperature. The energy contained in a mixture of air and most organic materials at the lower flammable limit is, generally, equivalent to approximately 52 British thermal units (Btu) per standard cubic foot (scf). At ambient temperature, then, the organic vapors and liquids in the air must provide at least 52 Btu per scf in order that a flame may be initiated by a high-temperature source and be self-sustaining. The oxidation reaction rate is a function of temperature, and oxidation can be carried out either above or below the auto-ignition temperature of a given vapor. An outside source of heat energy must be provided, however, to maintain the temperature and a specific reaction rate, unless (1) the concentration of the vapor is high enough to support self-sustained combustion and (2) an ignition source is maintained. Generally, high concentrations of combustibles are diluted to 25 percent or less of the lower flammability limit for safety. The required heat is then provided by independently burning a second source of fuel. The required technique, therefore, is to inject enough fuel gas into the air-rich effluent to bring a portion of the mass into the combustible range and thereby heat the remainder to the ignition temperature. The external energy thus added starts a chain reaction wherein heat from the burning vapors supplies a portion of the total heat required to complete the chemical reaction. Figures 3-1 and 3-2 show a direct-flame afterburner with provision for auxiliary heat.

Burning time is an important factor in afterburner design. This time period is called the "dwell time" or "residence time." It varies with the type of effluent and the method of incineration, being on the order of 0.3 to 0.6 second at 1,200° to 1,400°F. Burner type and arrangement have a considerable effect on burning time. The more thorough the flame contact is with the effluent gases, the shorter is the time required to achieve complete combustion. Turbulence in the combustor zone achieves much the same benefit of reducing required retention time, as actual flame contact. Multijet burners have been found to be very effective in securing good flame contact.

Figure 3-1 shows a burner arrangement wherein the effluent gases are used as both primary and secondary air for the multijet burners. Figure 3-2 shows a complete afterburner with this type of burner. Figure 3-3 illustrates a multijet burner arrangement in which no air is mixed with the gas prior to its injection into the combustion zone. The photograph shows the multiple small raw gas jets distributed over the duct area. This deployment of the jets results in efficient mixing of the effluent with the flame. Figure 3-4 shows an afterburner that incorporates a heat exchanger in which the afterburner exit gases are used to preheat the gas stream containing the pollutants that are to be burned.

If the combustion reaction is arrested by insufficient temperature, insufficient residence time, or poor mixing, CO, aldehydes, and other products of incomplete combustion may be produced. To achieve complete combustion, thorough mixing of the organic vapors and oxygen is required. Maintaining high turbulence or injecting steam promotes this intimate contact.

Properly designed and operated direct-flame afterburners usually achieve organic vapor removal efficiencies in excess of 95

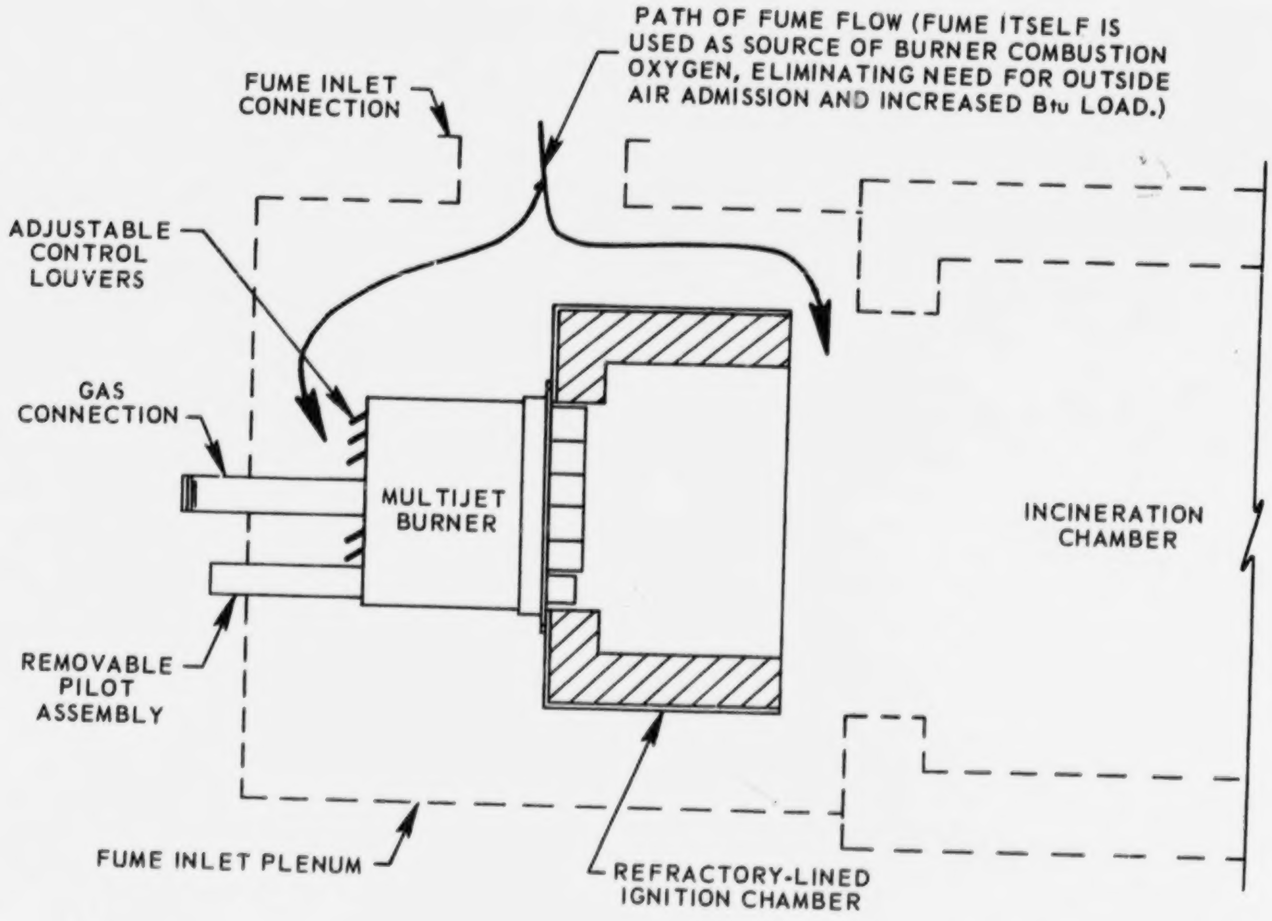

PATH OF FUME FLOW (FUME ITSELF IS USED AS SOURCE OF BURNER COMBUSTION OXYGEN, ELIMINATING NEED FOR OUTSIDE AIR ADMISSION AND INCREASED Btu LOAD.)
FUME INLET CONNECTION
ADJUSTABLE CONTROL LOUVERS
GAS CONNECTION
MULTIJET BURNER
INCINERATION CHAMBER
REMOVABLE PILOT ASSEMBLY
FUME INLET PLENUM
REFRACTORY-LINED IGNITION CHAMBER

Figure 3-1. Typical multijet burner arrangement used in direct-flame afterburners. (Courtesy Hirt Combustion Engineers)

percent. In the design of afterburners, burner utilization in conjunction with the overall combustor design must be considered to achieve the optimum and necessary time, temperature, and turbulence. The materials of construction, thicknesses, weights, etc., must, of course, be structurally adequate or thermal stress will lead to equipment failure.

3.2.1.2 Catalytic Afterburners

Catalytic afterburners are designed much like direct-flame types, but employ a solid active surface whereon the combustion reaction takes place, usually at a significantly lower temperature than would be required for combustion by direct flame. Since they can be operated at temperatures much lower than those required for direct-flame combustion, catalytic afterburners have the advantage of lower fuel costs in some applications. One type of catalytic afterburner is shown in Figure 3-5. Since fuel requirements for a direct-flame afterburner can be lowered by means of a heat exchanger, the total cost of operating a direct-flame afterburner may be comparable to the cost of operating the catalytic type.

Catalytic incineration can be applied to very low concentrations of contaminants, being limited only by the prescribed operating temperature limits of the catalyst and related equipment.

The primary problems with catalytic afterburners are their higher maintenance costs and their susceptibility to catalyst poisons. They will not function if the catalyst has become fouled by particulate matter, or if it

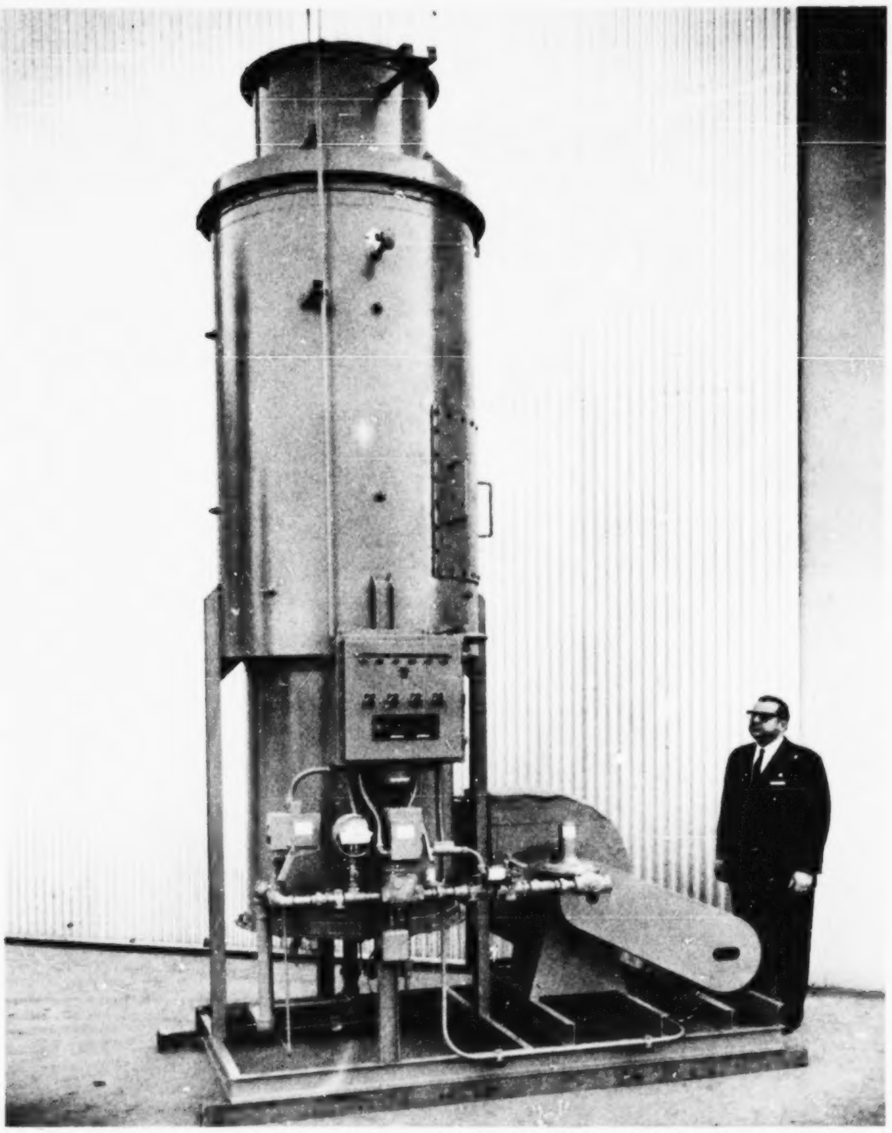
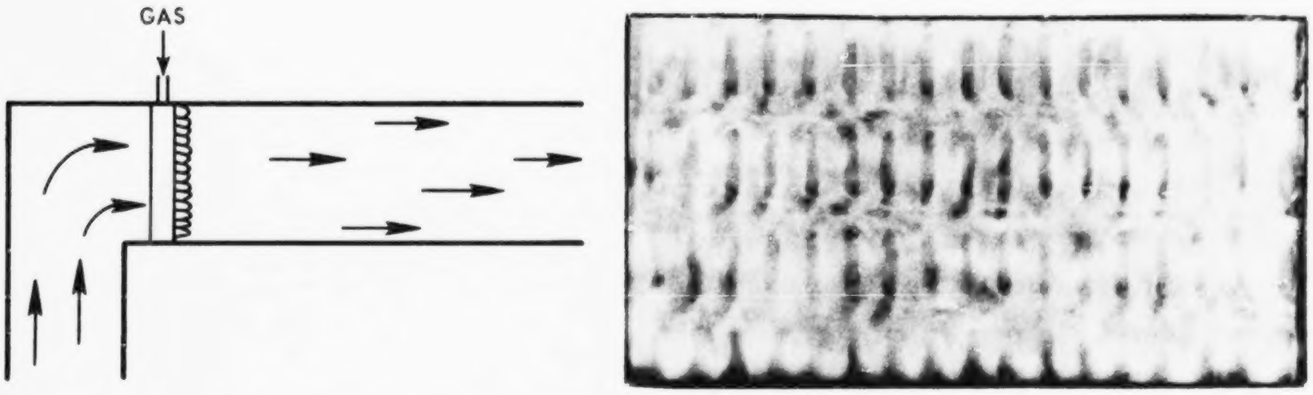


Figure 3-2. Direct-flame afterburner, vertical arrangement.
(Courtesy Hirt Combustion Engineers.)



a.

b.

Figure 3-3. Raw gas burner and multiple-jet grid. a. Diagram showing location of burner, b. Photograph of burner during operation. (Courtesy North American Manufacturing Company)

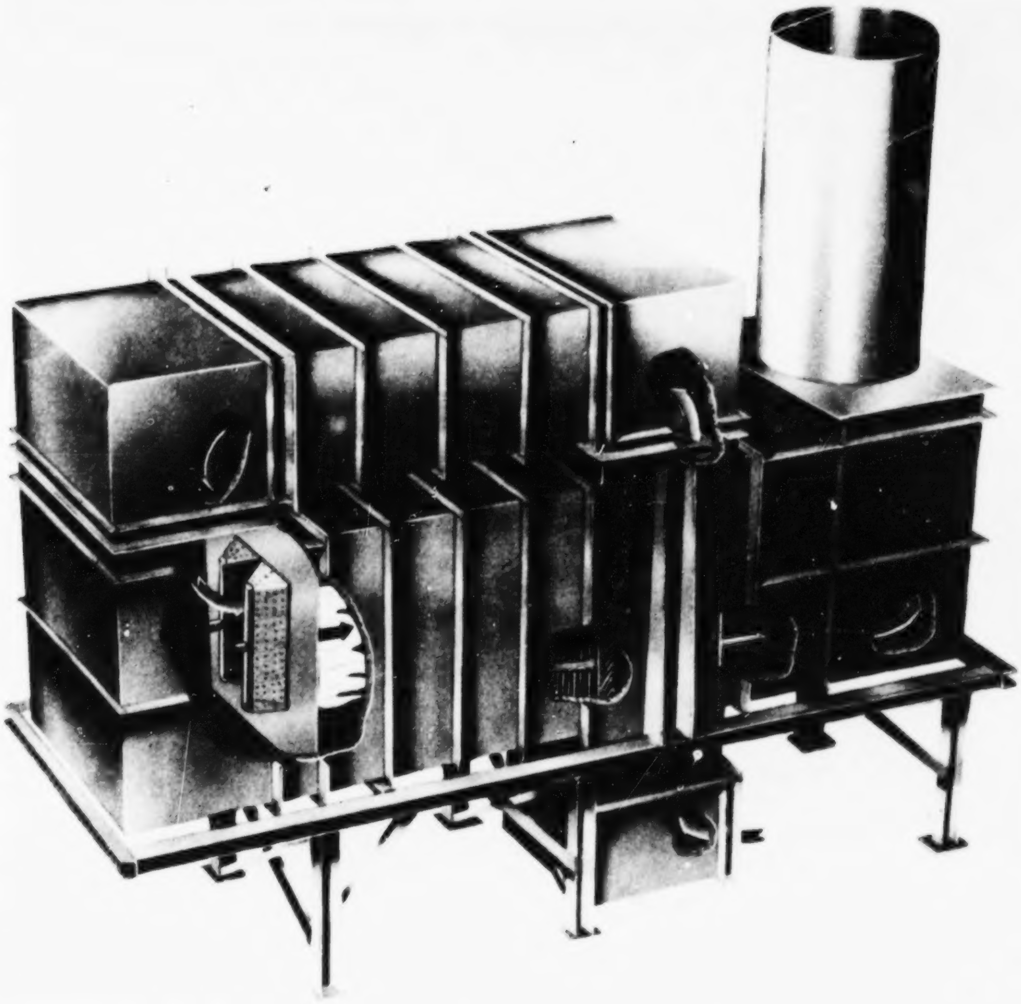


Figure 3-4. Afterburner with heat exchanger. (Courtesy The Air Preheater Company)

has been coated by polymers during low-temperature operation. Catalytic units therefore are not always inherently functional, and because of this, they may not meet prescribed standards of performance. An afterburner that does not achieve substantially complete combustion of the organic emissions can produce CO, aldehydes, and other partially oxidized substances. These materials may be less desirable than the emissions would be without an afterburner.

Catalyst life is, in general, greater than 2 years. Catalysts do, however, gradually lose activity through fouling and erosion of the surface. Loss of surface area and consequent reduction in activity can also be caused by heat effects.

Combustion catalysts consist of various shapes of basic material coated with a metallic compound. The variety of shapes and catalytic materials provide a multitude of catalysts for each application. As a result, a good general rule to follow is to consult with a catalyst manufacturer on the most suitable catalytic equipment configuration. Metallic and metallic compound coatings include platinum, platinum alloys, copper chromite, copper oxides, chromium, manganese, nickel, and cobalt. Base materials may be ceramic or metallic pellets or honeycombed forms.

Catalytic incineration has application in petroleum refining, chemical processing, foundry core baking, fabric coating, baking ovens, and others.

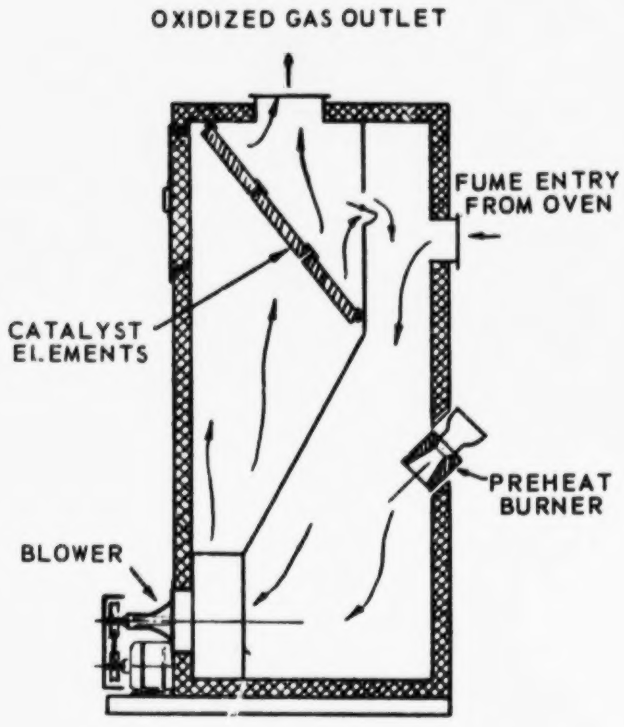


Figure 3-5. Catalytic afterburner. (Courtesy Catalytic Combustion Corporation)

3.2.1.3 Process Heaters and Boilers

Fireboxes of heaters and boilers can approximate the conditions of well-designed afterburners, providing the temperature, turbulence, and flame contact are adequate. If the gas stream to be treated contains appreciable heat, special fireboxes (waste heat boilers) are used. On the other hand, if the heat content is low, common types of steam and hot water heaters and boilers are used.

Completely satisfactory adaptations of boilers for use as afterburners are not common. All aspects of operation should be throughly evaluated before this method of air pollution control is used. The primary function of a boiler is to supply steam or hot water; and whenever its use as a control device conflicts with this function, one or both of its purposes suffer.

The use of a boiler as an afterburner requires that the following conditions[1] exist:

1. The air contaminants to be controlled must be almost wholly combustible since a boiler firebox cannot be expected to control noncombustible pollutants. Inorganic dusts and fumes deposit on heat transfer surfaces and foul them with resulting losses in boiler efficiency and steam-generating capacity.
2. The volumes of contaminated gases must not be excessive or they will reduce thermal efficiencies in much the same way as excess combustion air does. The additional volume of products of combustion will also cause higher pressure drops through the system, in some cases exceeding the draft provided by existing boiler auxiliaries.
3. The oxygen content of the contaminated gases when used as combustion air must be similar to that of air to insure adequate combustion. Incomplete combustion can form tars or resins which will deposit on heat-transfer surfaces and result in reduction of boiler efficiency. When these contaminants exceed air pollution control standards for gas- or oil-fired boilers, tube fouling will already have become a major maintenance problem.
4. An adequate flame must be maintained continuously in the boiler firebox. High-low or modulating burner controls are satisfactory, providing the minimum firing rate is sufficient to incinerate the maximum volume of effluent expected in the boiler firebox. Obviously a burner equipped with on-off controls would not be feasible.

3.2.2 Selection of an Afterburner

If an afterburner is being considered as a means of controlling organic contaminants, the following information about the application must be determined:

1. The chemical contaminant must be identified or tested to make sure it will burn completely, without yielding objectionable products of combustion. When objectionable products are

formed, the control system must employ equipment in addition to afterburners.

2. The concentration and physical form of the contaminant must be determined. These determinations help provide estimates of the available heat to be supplied. If liquid mists or solid materials are present, they may preclude the use of catalytic afterburners, or fireboxes of heaters and boilers.
3. The temperature of the effluent to be controlled is required, to help determine the needed auxiliary heat and fuel and the final volume of gases in the afterburners.
4. The volume rate of the effluent is required to set the rate of auxiliary fuel and determine the dimensions of the afterburner. Throat velocities of 15 to 25 feet per second (ft/sec) have been found to provide adequate mixing of contaminated gases with flames of burner combustion products. Where a single-nozzle burner is used, velocities of 40 ft/sec have been used to enhance turbulence and mixing. Combustion-chamber velocities, on the other hand, are usually held at 10 to 15 ft/sec to allow sufficient residence time and sufficient turbulence for complete combustion while maintaining a reasonable length for the afterburner.
5. The oxygen content of the effluent must be known to determine whether there will be sufficient quantity for complete combustion of the contaminants and any extra fuel.
6. The space limitations must be considered in designing the afterburner.
7. Weight limitations must be considered, because afterburners may be large enough and heavy enough to require additional structural support.
8. The recovery of heat should be considered, since this heat is the only thing of value that can be recovered from an incinerator.
9. The cost of electric power and gaseous fuels must be considered because they contribute significantly to the total operating costs of the equipment.

3.3 ADSORPTION

3.3.1 Introduction

The property of a surface to collect vapors is known as adsorption. Gas-purification processes involving this principle are based upon the physical properties of certain granular solids, known as adsorbents, by which they attract selected components of a fluid and retain them on their surfaces. The amount of adsorption on the surface of most solids is small; however, certain materials (e.g., activated alumina, silica gel, and activated carbon) have been developed to adsorb substantial quantities of gases and vapors on their surfaces. These materials are highly porous and have a very large surface-to-volume ratio. A fluid is able to penetrate the material and contact the large surface area available for adsorption.

Complete package adsorption systems are available from a number of manufacturers for use in processes involving volatile solvents.

This section presents the basic operating principles and applications of adsorption. Types of adsorbents and equipment are also discussed.

3.3.2 Basic Operating Principles

There are two main types of adsorption: (1) physical adsorption in which the gas is attracted to the surface of the adsorbent and (2) chemical adsorption in which the gas interacts with the adsorbent in the manner of a chemical reaction.[2] The surface attraction is due to van der Waals' forces, the intermolecular forces that produce normal condensation to the liquid state. On a smooth surface, van der Waals' adsorption gives a layer not more than a few molecules thick. Within the capillaries of a porous solid, however, this surface adsorption is supplemented by capillary condensation. As a result, the total amount adsorbed is substantially increased.

In vapor-phase adsorption, essentially an exothermic gas-solid equilibrium process, the approach to equilibrium is governed by the rate of adsorption. As such, conditions that shift the equilibrium toward saturation usually improve the process. Consequently, the system is more efficient near the dew point of the adsorbate (substance being absorbed), and a vapor-phase adsorption system generally should operate at the highest pressure and the lowest temperature within the process limitations.[3]

After some period of usage, the adsorbent will become saturated with the contaminant and will no longer function. When this occurs, it must be regenerated or replaced. Regeneration may be done in a number of ways. The temperature of the adsorbent may be raised until the vapor pressure of the adsorbed gas exceeds atmospheric pressure. The adsorbed gas will then be evolved and may be collected at atmospheric pressure. The most common method is to withdraw the adsorbed gas in a stream of easily condensable gas such as steam. The stripped gas is then recovered by condensing the mixture. Thus by regeneration, the adsorbent is restored to activity, and the adsorbed material is removed for disposal or recovery. An inert gas can also be used as a stripping agent.

If the gas or vapors to be adsorbed consist of not one but several compounds, the adsorption of the various components is not uniform. Generally, these components are adsorbed in an approximate inverse relationship to their volatilities. Hence, when air containing a mixture of organic vapors is passed through a bed of adsorbent, the vapors are equally adsorbed at the start; but as the amount of the higher-boiling constituent retained in the bed increases, the more volatile component revaporizes. The point at which the rate of adsorption of the more volatile component starts to decrease is called a "breakpoint." After this breakpoint is reached, the exit vapor consists largely of the more volatile material. The higher-boiling component has displaced the lower-boiling component, and this is repeated for each additional component.

The main function of the adsorption equipment is to bring the gas and solid adsorbent into direct contact to facilitate adsorption. Two or more adsorbers are required for continuous adsorption, one or more being in operation while the other is being regenerated. Fluidized bed and moving bed equipment may be used for large-scale continuous operation.

3.3.3 Applications of Adsorption

While, in general, fixed-bed adsorbers have not been installed to recover organic solvent vapors when the vapor-laden stream contained less than 0.2 pound of solvent per 1,000 scf of gas (2,700 ppm), much lower concentrations can be actually recovered very efficiently. This is because adsorption is virtually complete and independent of concentration; however, the maximum bed loading (saturation point) is dependent on initial concentration.

There is a range of vapor concentration for which profitable recovery of organics cannot be obtained with either regenerative or nonregenerative adsorption. This range, between a few ppm and about 1,000 ppm, is often unsuitable for nonregenerative systems because of the high cost of adsorbent replacement. It is also uneconomical for regenerative systems because adsorbate recovery costs generally exceed the value of the material recovered.[4] For such a range, instead of desorption, newly developed oxidative destruction of the adsorbate is suggested. The carbon is impregnated with a small amount of catalyst, which is inactive during adsorption. It may be activated by heating the air stream, thus bringing about catalytic oxidation of the adsorbate.

For satisfactory adsorption, a substance should have a molecular weight greater than 45. Methanol is the only common organic solvent that does not meet this requirement.

Since corrosion is a problem in some applications, especially when steam is used for regeneration, systems are sometimes constructed of stainless steel.

Despite its disadvantages, adsorption appears to be the most economical control method for organic vapors in the concentration range of 100 to 200 ppm when compared to other methods of emission control.[5]

Processes that discharge organic vapors that can be controlled by adsorption include dry cleaning; degreasing; paint spraying; tank dipping; solvent extracting; metal foil coating; plastics, chemical, pharmaceutical, rubber, linoleum, and transparent wrapping manufacturing; and, fabric impregnation. In the manufacture of paints and varnishes, adsorption of the solvents followed by their recovery is not feasible alone, because of the fouling of the absorbent with coating solids. Scrubbing with water to remove the paint solids and condensables should precede adsorption of the solvent by carbon.[6]

3.3.3.1 Types of Adsorbents

The most important characteristics of solid adsorbents are their large surface-to-volume ratios and their preferential affinity for certain specific substances. The preferential adsorption characteristics and physical properties of industrial adsorbents determine the applications for each type. All the adsorbents are capable of adsorbing organic solvents, impurities, and water vapor from gas streams, but each has a particular affinity for either polar or nonpolar vapors.[7]

Water vapor is an example of a polar compound, and organic vapors are nonpolar. The siliceous and metal oxide adsorbents have an affinity for polar compounds; activated carbon is the most commonly used nonpolar adsorbent.

Silica gel and aluminum oxide preferentially adsorb water from a gas mixture containing water vapor and organic solvents. This is a serious disadvantage in emission control where the water content of the gas stream is often greater than the organic vapor content. Silica gel and activated alumina disintegrate in the presence of liquid water, hence wet steam may not be used for desorption. These adsorbents are used successfully, in the drying of water-saturated solvents recovered by decantation.

Activated carbons adsorb organic vapors from gases selectively, even in the presence of water vapor, and, therefore, are widely used for gas purification and organic vapor recovery. The great advantage that activated carbon has over other adsorbents in the field of emission control is its outstanding ability to recover organic solvents from low concentrations in the presence of water vapor. A list of vapors that can be adsorbed by activated carbon is presented in Table 3-1.

Activated carbons for use as gas adsorbents are manufactured from coconut shells, fruit pits, coal, peat, and petroleum residues.[8] The raw materials are first carbonized by selective oxidation of the carbonaceous material by air at low temperature. The hard materials are crushed to size and activated directly to give hard dense granules of carbon. The softer materials are ground to a powder, formed into briquettes or pellets with a tar or pitch binder, calcined, crushed to size, and then activated. Activation consists of heating to 1560° to 1740° F with steam, carbon dioxide, or flue gas.

Gas purification application, involving the removal of small quantities of impurities such as those listed, include deodorizing of air, the removal of odors in ventilation systems of buildings, and the removal of dangerous toxic vapors from air streams.

3.3.4 Types of Adsorption Equipment

3.3.4.1 Description of an Adsorption Process

A typical adsorption process is shown diagrammatically in Figure 3-6. One adsorber handles the vapor-laden stream while the other is undergoing regeneration. When the first, or onstream, adsorbent bed approaches the break-through point, the second adsorber, which meanwhile has been regenerated, is placed on stream. This procedure insures that the vapor is removed from the air continuously. Caution must be exercised to insure that an adsorber is adequately cooled after desorption before it is placed on stream again. Contact of organic vapors with a hot carbon

Table 3-1. REPRESENTATIVE GASES AND VAPORS SELECTIVELY ADSORBED BY ACTIVATED CARBON

1. acetaldehyde
2. acetone
3. benzene
4. isobutane
5. normal butane
6. normal butene
7. butyne
8. carbon dioxide
9. carbon disulfide
10. carbon tetrachloride
11. carbonyl sulfide
12. chloroform
13. cumene
14. cyclohexane
15. cyclohexanone
16. cyclopentadiene
17. dichloroethane
18. dichloroethylene
19. dimethyl formamide
20. ethane
21. ethanol
22. ethyl acetate
23. ethyl chloride
24. ethyl mercaptan
25. ethylene
26. ethylene oxide
27. freon 12
28. heptane
29. normal hexane
30. hexanol
31. hydrogen cyanide
32. hydrogen sulfide
33. isopentane
34. isoprene (methyl butadiene 1,3)
35. isovaleric acid
36. simulated kerosene ($C_{14}H_{30}$)
37. methane
38. methyl ethyl ketone
39. methyl mercaptan
40. mineral spirits
41. neopentane
42. normal pentane
43. perchloroethylene
44. propane
45. propylene
46. propyl mercaptan
47. pyridine
48. tetrahydrofuran
49. tetrahydrothiamine
50. toluene
51. trichloroethylene
52. vinyl chloride
53. metaxylene

bed may promote decomposition or partial oxidation and thereby result in the discharge of odorous or irritating gases to the atmosphere.[4]

Adsorbers may be classified as regenerative or nonregenerative. Regenerative systems are used when the adsorbent is to be reactivated by desorption and the desorbed vapors recovered for reuse or disposal. Nonregenerative systems are used when the adsorbent is to be replaced with fresh material, the displaced material usually being returned to the vendor for regeneration. Nonregenerative adsorption is often employed in air-conditioning systems for large buildings.

Adsorbers can have fixed, moving, or fluidized beds. They can be set vertically or horizontally. A single fixed-bed unit is satisfactory if process downtime is available for regeneration of the adsorbent. For example, an adsorber for a spray-paint booth that is in use only 6 hours a day can be designed to extract the total emission for this period and to be desorbed after the operating period.

The simplest equipment for a fixed-bed adsorber is a vertical cylindrical vessel fitted with perforated screens that support the carbon. Another type of fixed bed is arranged in the shape of a cone, as shown in Figure 3-7. The cone shape allows more surface area for

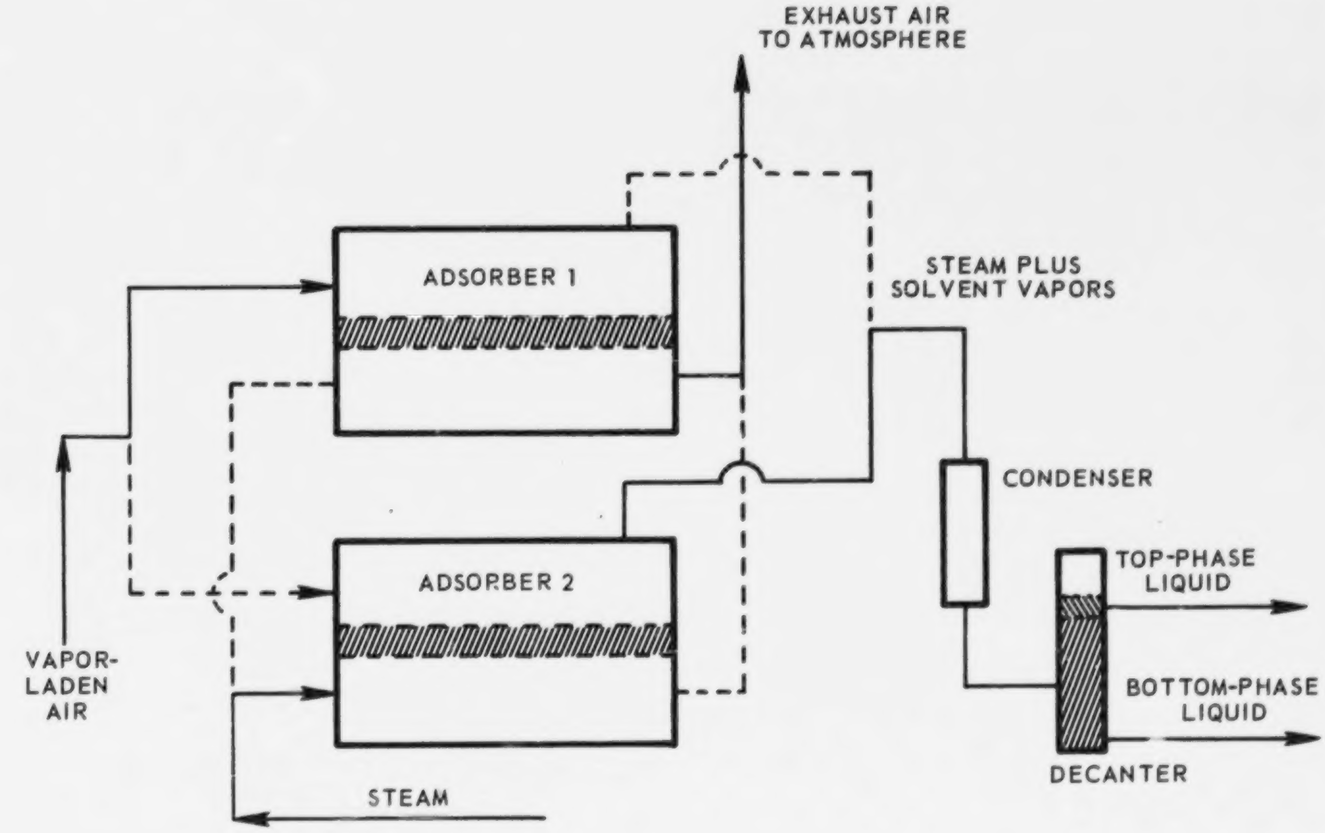

EXHAUST AIR
TO ATMOSPHERE
ADSORBER 1
STEAM PLUS
SOLVENT VAPORS
CONDENSER
ADSORBER 2
TOP-PHASE
LIQUID
VAPOR-
LADEN
AIR
BOTTOM-PHASE
LIQUID
DECANTER
STEAM

Figure 3-6. Diagrammatic sketch of two-unit fixed-bed adsorber.

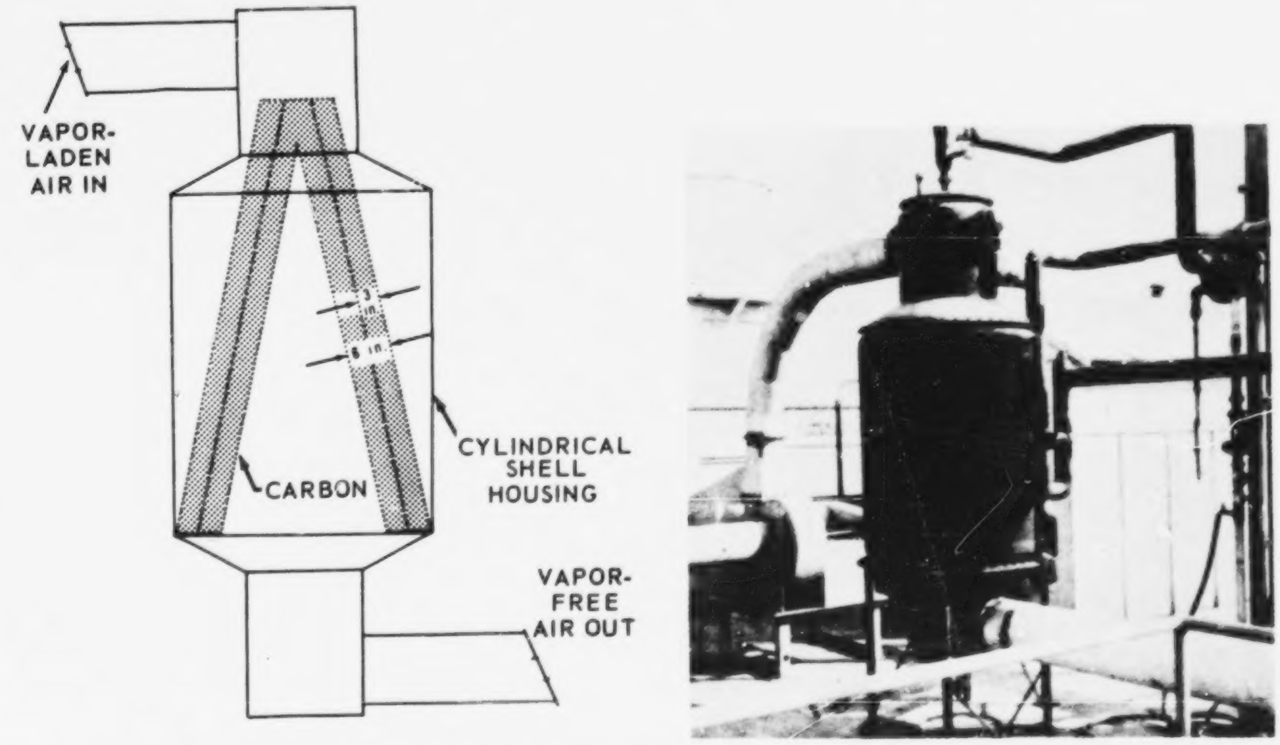

VAPOR-
LADEN
AIR IN
3 in.
6 in.
CYLINDRICAL
SHELL
HOUSING
CARBON
VAPOR-
FREE
AIR OUT

Figure 3-7. Left: Diagrammatic sketch of vertical adsorber with two cones, permitting studies on different depths of carbon beds. Right: Vertical cone adsorber in operation.

gas flow and accommodates higher air rates at lower pressure drops than does a flat bed of the same diameter using the same total weight of adsorbent. Where the cone shape will provide adequate adsorption, its use tends to reduce costs of moving the gases through the system. A commercially available, skid-mounted unit is shown in Figure 3-8.

Moving-bed adsorbers actually move the adsorbent into and out of the adsorption zone. The fluidized-bed adsorber contains a number of shallow fluidized beds of activated adsorbent. The air flows upward through these beds and fluidizes them; the solvent is progressively adsorbed onto the carbon. Solvent-free air is finally discharged into the atmosphere through dust collectors at the top of the adsorber vessel. Fresh adsorber is fed onto the top tray of the adsorber, into the fluidized bed. It flows across the tray, over a weir, and down a downcomer to the tray beneath, progresssively becoming loaded with solvent as it moves through the adsorber. Because the carbon circulation rate can be closely matched to the solvent feed rates, very high loading of solvent on carbon can be achieved. This can result in lower steam consumption for desorption. The fluidized state, if properly used, tends to avoid the channeling problem sometimes encountered with fixed beds.

3.3.4.2 Factors Involved in Selection of an Adsorber

Consideration of the proper type of adsorber begins with identifying the components of the air stream to be treated, the stream temperature, pressure, water content, and flow rate. If any solids are present, they may have to be removed to prevent fouling of the adsorbent surface.

With this information, a general idea of the amount of adsorbent required can be obtained from "adsorption isotherms," graphs of amount adsorbed versus vapor pressure. These relationships, often available in the literature, actually show the quantity adsorbed per unit weight of adsorbent under true static equilibrium conditions. In air pollution control, however, most organic emissions are very dilute vapors that flow over

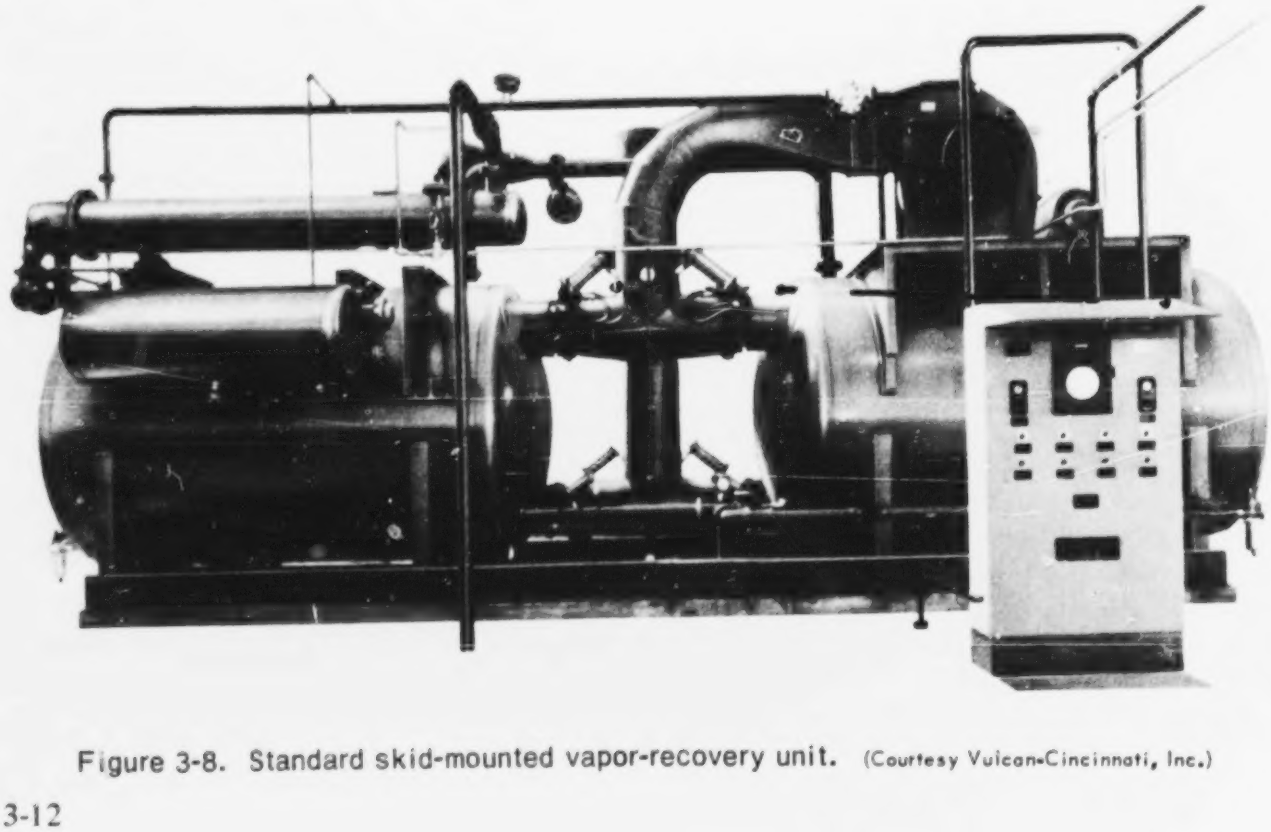


Figure 3-8. Standard skid-mounted vapor-recovery unit. (Courtesy Vulcan-Cincinnati, Inc.)

the adsorbent and are in contact with the surface only momentarily. Consequently, this removal process involves mass transfer as well as adsorption, and no adequate design and scale-up procedure is available.[1]

In actual practice, the adsorptive capacity, height of bed, and stripping conditions for a given adsorption problem are obtained experimentally in laboratory (or pilot) units. For example, pilot plant studies have shown that for optimum use of activated carbon to control toluene vapors, stripping should be taken to the point where 8½ pounds of toluene is recovered from each 100 pounds of carbon instead of attempting to remove 20 pounds, which is possible under very prolonged and uneconomic contacting and stripping.[9]

When the basic information concerning the stream to be treated is established and the adsorbent to treat it is selected, the type and size of adsorber can be determined. For many processes that discharge organic vapors into the air, the packaged equipment available is suitable if certain precautions are taken.

3.3.5 Instruments for Control of Adsorption Process

Vapor concentration and adsorber temperature are the most important factors in the control of an adsorption process. The concentration of the vapor fed to the adsorber must be kept at a safe level, which may be calculated from a knowledge of the quantity of air or gas being drawn through the adsorption system. In most cases, the rate of solvent evaporation is measurable, and a simple orifice-type flow meter is sufficient to enable calculation and maintenance of the desired concentration.

The low concentrations in the effluent of the adsorber may be measured in a number of ways, depending upon the physical and chemical properties of the solvent:

1. The vapor may be adsorbed. A small measured volume of the vapor-laden air is passed through a small test adsorber; the adsorbent is then steamed, and the solvent is condensed, collected, and weighed.
2. Vapors may be detected by qualitative analysis. For example, chlorinated vapors may be decomposed by passing them through a quartz tube heated to more than 400° C; the chlorine is then detected with a 2 percent potassium iodide solution.
3. Vapors may be measured quantitatively. The solvent is taken into solution and titrated, using an appropriate indicator.
4. The vapors may be measured by instrumental methods such as infrared absorption, gas chromatography, or atomic-absorption spectroscopy. Unlike chemical quantitative analysis, which is often lengthy and unsuitable for routine or continuous control, these methods are capable of accurately detecting a few-part-per-million concentration in a gas mixture.

The instrumental methods are best for pollution control purposes. Some instrumental analyzers may be used continuously to monitor selected components from one or several process streams such as measurement of solvent concentration at various points, in the plant and building, as well as the concentration at the inlet and outlets of the adsorbers.

The temperature should be measured by placing temperature sensors at strategic points in the solvent air line and in the carbon bed. Recording temperature devices may be used so that temperature variations may be noticed by the operators. Generally, a change in the condition of the adsorbent is reflected as a change in the operating temperature.

The ventilation system and recovery units must be designed by experienced contractors to insure as safe a final system as possible, because adsorption is the process often used to collect flammable or toxic substances. All usual precautions for handling toxic or flammable solvents must be observed. If necessary, flame arrestors should be placed so as to prevent the spread of flame or an explosion through feed lines to the adsorber.

If raised to the ignition temperatures and exposed to oxidizing conditions, activated carbon burns readily. The majority of carbons are safe, however, for operation in air temperatures below 300° F.[7]

3.4 ABSORPTION

3.4.1 Introduction

In the absorption process a soluble component of a gas mixture is dissolved into a relatively nonvolatile liquid. In addition to being simply dissolved, the gas mixture may react chemically with the liquid. This technique is quite common and profitable as a step in petroleum and petrochemical operations in which a gas has a relatively high concentration of solvent vapor. From an air pollution standpoint, absorption has been used primarily to control inorganic compounds, rather than organic vapors, because low concentrations of organic vapors tend to require long contact time and large quantities of absorbent. The economics of the method under these circumstances are often unfavorable unless the absorbent can be regenerated or the solution can be used as a process make-up stream. Otherwise, the absorbent stream can present an additional disposal problem. In emission control applications, absorption is best used in conjunction with other control techniques such as incineration or adsorption, as required, to achieve the prescribed degree of emissions removal.

3.4.2 Applications

Absorption of hydrocarbons in the petroleum and petrochemical industries is an important manufacturing step. Products often absorbed in a product-recovery step in industrial processes include light hydrocarbons (e.g., acetylene, butadiene), acetic acid, methanol, ethanol, propanol, chloroform, formaldehyde, formic acid, amines, and ketones. Actually, this type of absorption must be considered as a preliminary step in air pollution control as it does not usually remove as much of the material as would be required for emission control.

Absorption has been employed in scrubbers to remove condensable vapors and particulate matter from the following sources: asphalt batch plants, ceramic tile manufacture, coffee roasters, chromium-plating units, petroleum coker units, fish meal systems, pipe coating, smoke generators and smoke houses, and varnish and resin cookers.[10-12]

3.4.3 Selection of an Absorbent

The ideal absorbent should meet six requirements:

1. The gas should be quite soluble to enhance the rate of absorption and to decrease the quantity of absorbent required. Solvents that are chemically similar to the solute generally provide good solubility.
2. The solvent should be relatively nonvolatile.
3. The solvent should be noncorrosive, if possible, to reduce equipment costs.
4. The solvent should be inexpensive and readily available.
5. The solvent should have low viscosity to increase absorption and reduce flooding.
6. The solvent should be low in toxicity, nonflammable, and chemically stable, and have a low freezing point.[1]

The common absorbents for organic vapors are water, mineral oil, nonvolatile hydrocarbon oils, and aqueous solutions (e.g., solutions of oxidizing agents, sodium carbonate, or sodium hydroxide).

3.4.4 Types of Absorbers

Gas absorption equipment is designed to provide thorough contact between the gas and the liquid solvent to permit interphase diffusion of the materials. This contact is provided by several types of equipment; namely, bubble-plate columns, jet scrubbers, packed towers, spray towers, and venturi scrubbers.[13] Bubble-plate columns employ stepwise contact by means of a number of plates or trays arranged so that the gas is dispersed through a layer of liquid on each plate, as shown in Figure 3-9. Each plate is more or less a separate stage, and the number of plates

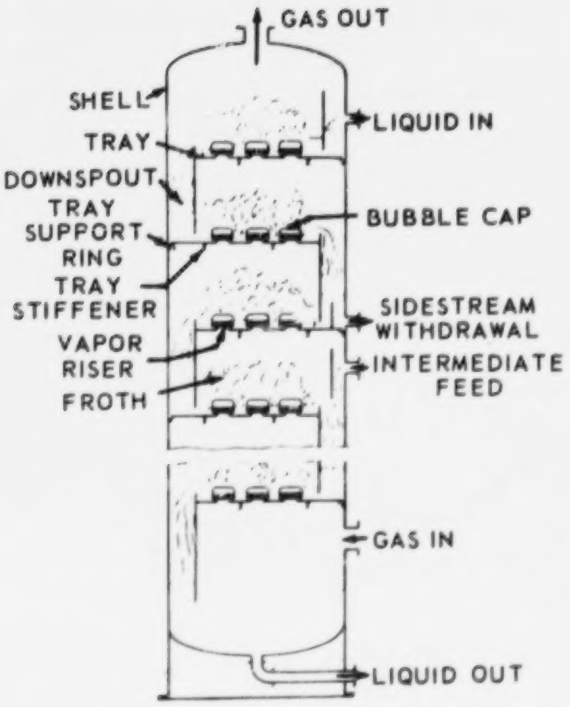

GAS OUT
SHELL
LIQUID IN
TRAY
DOWNSPOUT
TRAY SUPPORT RING
BUBBLE CAP
TRAY STIFFENER
SIDESTREAM WITHDRAWAL
VAPOR RISER
INTERMEDIATE FEED
FROTH
GAS IN
LIQUID OUT

Figure 3-9. Schematic diagram of a bubble-cap tray tower.[14]
(Courtesy of McGraw-Hill Book Co.)

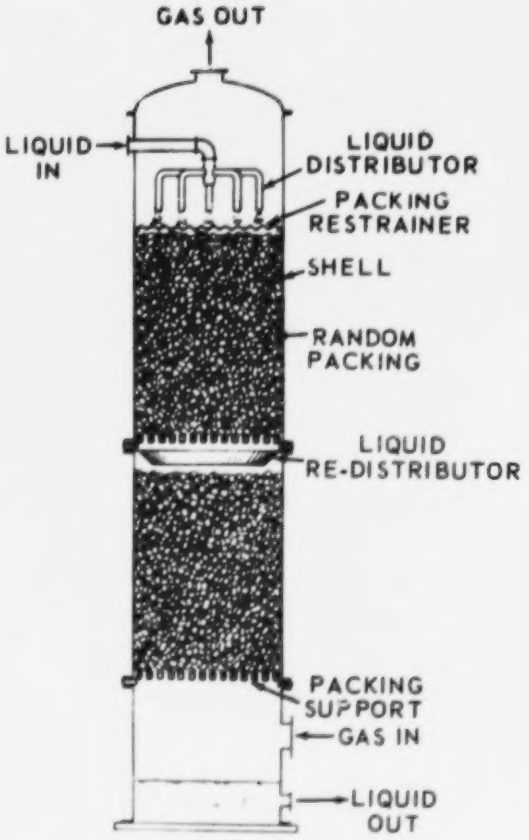

GAS OUT
LIQUID IN
LIQUID DISTRIBUTOR
PACKING RESTRAINER
SHELL
RANDOM PACKING
LIQUID RE-DISTRIBUTOR
PACKING SUPPORT
GAS IN
LIQUID OUT

Figure 3-10. Packed tower.
(Courtesy of McGraw-Hill Book Co.)

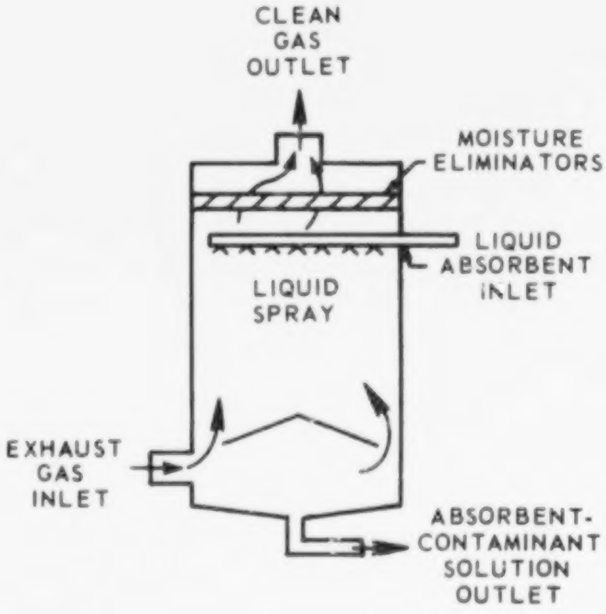

CLEAN GAS OUTLET
MOISTURE ELIMINATORS
LIQUID ABSORBENT INLET
LIQUID SPRAY
EXHAUST GAS INLET
ABSORBENT-CONTAMINANT SOLUTION OUTLET

Figure 3-11. Spray tower.

required depends upon the difficulty of the mass transfer operation and the degree of separation desired. Jet scrubbers are basically spray nozzles. Packed towers are filled with a packing material having a large surface-to-volume ratio; the packing is wetted by the absorbent to provide a large surface area of liquid film for continuous contacting of the gases (Figure 3-10). Spray towers (Figure 3-11) dispense the liquid in the form of a spray and pass the gas through this spray. Venturi scrubbers contact the gas and the absorbent in the throat of a venturi nozzle (Figure 3-12). The gas-liquid mixture then enters an entrainment separator tangentially, and centrifugal force separates the liquid droplets from the gas.

Packed and spray towers are most often used because they introduce relatively lower pressure losses than the bubble-plate columns. Low pressure losses are important because large volumes of exhaust gases with relatively low concentrations of contaminants are treated in many air pollution control installations. Spray chambers have the advantage of

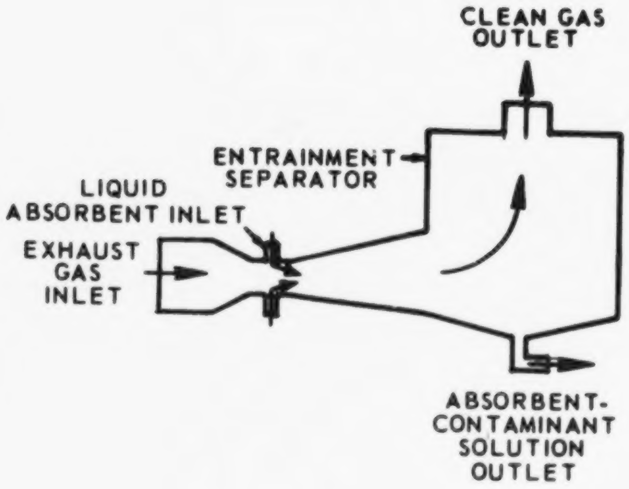


Figure 3-12. Venturi scrubber.

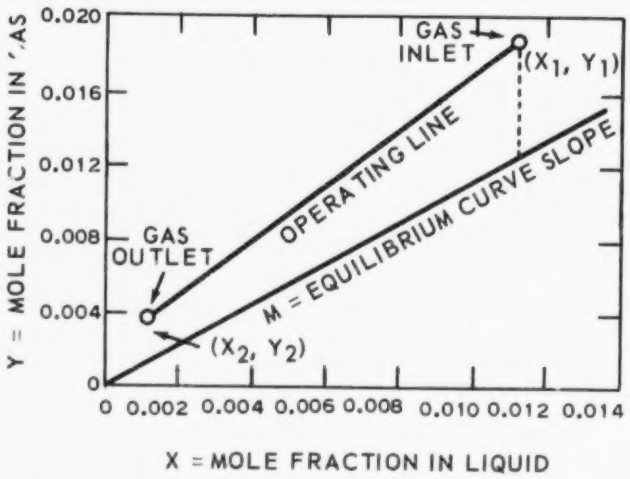


Figure 3-13. Driving force for absorption.

being able to handle exhaust gases containing particulate matter without plugging. The spray chamber is, however, the least effective of the various types of absorption equipment. Since very fine droplets of liquid are necessary for good contact, spray nozzles operated with high pressure drop are required. These fine droplets tend to be entrained in the gas and must be separated.

3.4.5 Principles of Operation

Absorption of a gaseous component by a liquid occurs when the liquid contains less than the equilibrium concentration of the component. This departure of the liquid stream from equilibrium provides the driving force for absorption.[15] As illustrated in Figure 3-13, for a given liquid concentration, the gas concentration in the tower is always greater than the corresponding equilibrium concentration.

The rate of absorption depends upon (1) the temperature, diffusivity, viscosity, and density of the substance; (2) the tower conditions, particularly the gas and liquid mass flow rates; and (3) the kind of packing employed. These factors and equilibrium data have been correlated to give two key measures of tower performance, the number of transfer units and the height of a transfer unit.[14] The number of transfer units is the number of times the driving force (the departure from equilibrium) must be divided into the prescribed change in gas concentration. The height of a transfer unit is the depth of packing needed to effect one transfer unit. When the height of a transfer unit is multiplied by the number of units, the required height of packing in the absorption tower is estimated. Procedures for carrying out these calculations are given in the Air Pollution Engineering Manual.[1] A simple countercurrent tower is limited in effectiveness to one transfer unit, and enrichment of the liquid phase is equal to the driving force producing the enrichment.

Packed towers can provide as many transfer units as is practical. The gases and liquids are normally contacted in counter flow to achieve maximum absorption efficiency, but they can also be contacted in parallel flow.

The packing should provide a large surface area and should give enough void space when packed to permit good liquid flow. The material should not break easily in handling and should be light in weight; it should be chemically inert enough to prevent deterioration. Manufactured packing has various shapes, as shown in Figure 3-14. Raschig rings, consisting of hollow cylinders having an external diameter equal to the length, are the most common type of packing.

In most emission control cases, the concentrations involved range so low that the equilibrium curve and the operating curves are essentially straight lines. An estimate of the

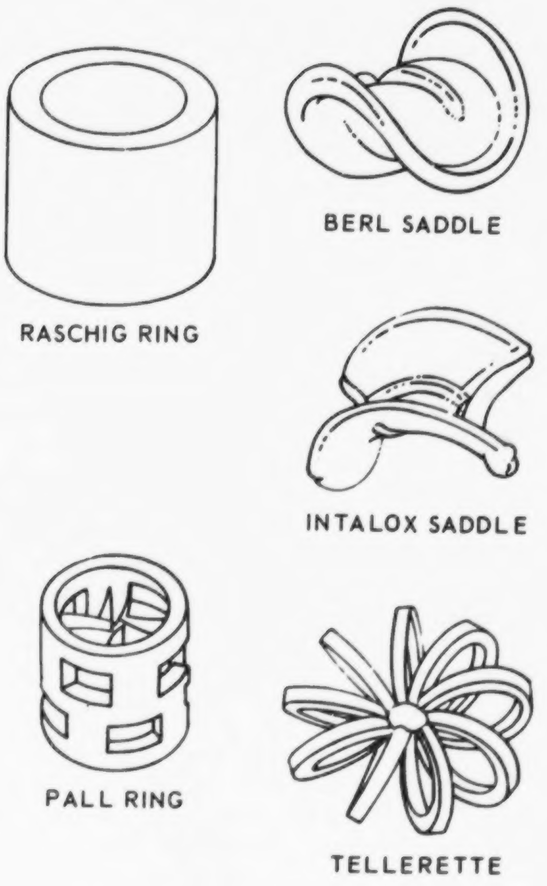


Figure 3-14. Common tower packing materials.

size of an absorber can usually be made under these circumstances in three steps:

1. The mass flow rates per square foot of tower area are determined by using information supplied for the packing selected (Table 3-2). These prescribed flows will permit the tower to operate without flooding. From these values and the quantity of exhaust stream to be treated, the tower cross-sectional area is obtained.
2. The number of transfer units, N, is determined through the use of Figure 3-15. First, convert the liquid and the gas flows, L and G, from pounds per hour to moles per hour; then take their ratio (liquid/gas). Divide this by the slope of the equilibrium line (shown as m, Figure 3-13). The result is the value "A" used as a label for each curve of Figure 3-15. The required ordinate is simply the outlet gas concentration (in mole fraction units) divided by the inlet concentration, since the incoming absorbent usually contains no absorbate (x_2=0).

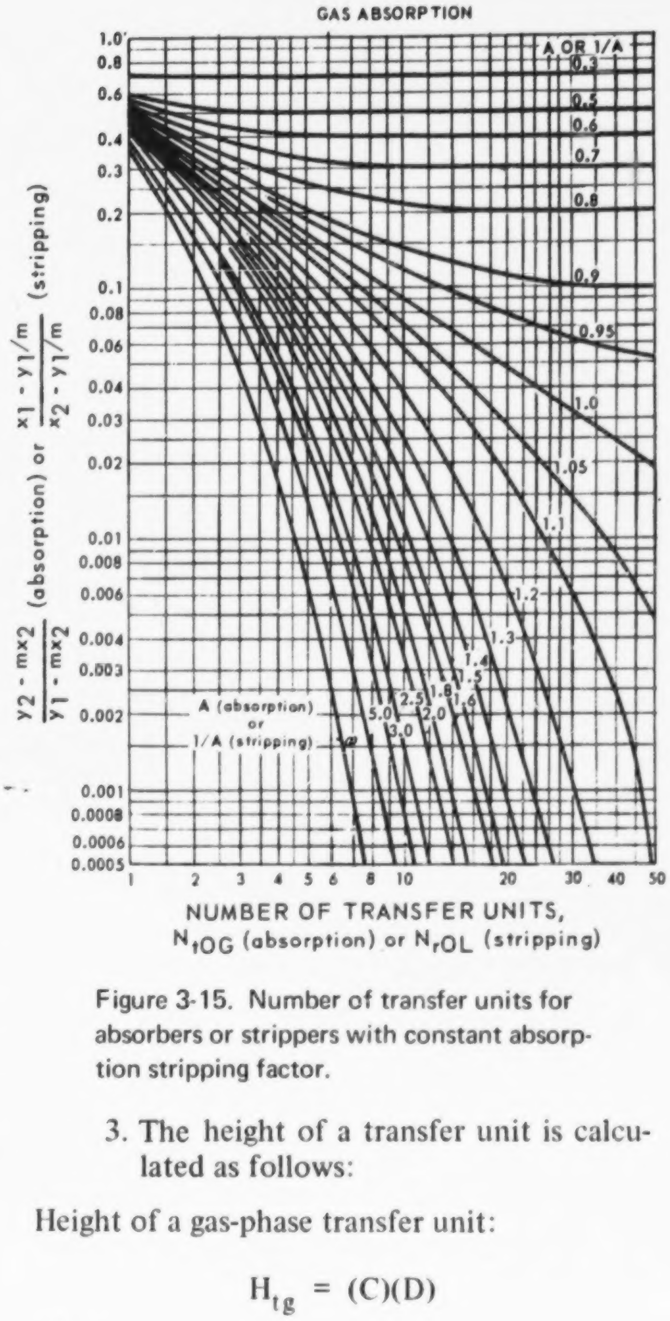


Figure 3-15. Number of transfer units for absorbers or strippers with constant absorption stripping factor.

3. The height of a transfer unit is calculated as follows:

Height of a gas-phase transfer unit:

$$H_{tg} = (C)(D)$$

where:

$$C = \frac{\alpha(\text{gas rate, lb/hr-ft}^2)^\beta}{(\text{liquid rate, lb/hr-ft}^2)^\gamma}$$

$$D = \frac{(\text{gas viscosity, lb/hr-ft})}{(\text{gas density, lb/ft}^3)\ (\text{diffusivity, ft}^2/\text{hr})}$$

Table 3-2. CONSTANTS FOR USE IN DETERMINING GAS-PHASE HEIGHT OF TRANSFER UNITS[a,14]

Packing	α	β	γ	Gas flow rate, lb/hr-ft^2	Liquid flow rate, lb/hr-ft^2
Raschig rings					
3/8 in.	2.32	0.45	0.47	200 to 500	500 to 1,500
1 in.	7.00	0.39	0.58	200 to 800	400 to 500
	6.41	0.32	0.51	200 to 600	500 to 4,500
1-1/2 in.	17.30	0.38	0.66	200 to 700	500 to 1,500
	2.58	0.38	0.40	200 to 700	1,500 to 4,500
2 in.	3.82	0.41	0.45	200 to 800	500 to 4,500
Berl saddles					
1/2 in.	32.40	0.30	0.74	200 to 700	500 to 1,500
	0.81	0.30	0.24	200 to 700	1,500 to 4,500
1 in.	1.97	0.36	0.40	200 to 800	400 to 4,500
1-1/2 in.	5.05	0.32	0.45	200 to 1,000	400 to 4,500
Partition rings					
3 in.	650	0.58	1.06	150 to 900	3,000 to 10,000
Spiral rings (stacked staggered)					
3 in. single spiral	2.38	0.35	0.29	130 to 700	3,000 to 10,000
3 in. triple spiral	15.60	0.38	0.60	200 to 1,000	500 to 3,000
Drip-point grids					
No. 6146	3.91	0.37	0.39	130 to 1,000	3,000 to 6,500
No. 6295	4.56	0.17	0.27	100 to 1,000	2,000 to 11,500

[a] Courtesy of McGraw-Hill Book Co.

The diffusivity is that of the component in the gas stream. Height of liquid-phase transfer unit:

$$H_{tL} = \phi(E)(F)$$

where:

$$E = \left[\frac{(\text{liquid rate, lb/hr-ft}^2)}{(\text{liquid viscosity, lb/ft-hr})}\right]^{\eta}$$

$$F = \frac{(\text{viscosity of the liquid, poises})}{(\text{liquid density, g/cm}^3)\ (\text{comp. liq. diffusivity, cm}^2/\text{sec})}$$

Values for α, β, γ are given in Table 3-2. Values for ϕ and η are given in Table 3-3.

From these, the height of an overall transfer unit is:

$$H_{tO} = H_{tg} + H_{tL}/A$$

With the number of transfer units estimated, and the height of each, the packing height is then estimated as the product of the two:

$$\text{Packing height} = (N)(H_{tO})$$

The packed column requires a blower and motor to overcome its pressure drop. Pressure drop data show considerable variation, presumably due to differences in packing density. An empirical correlation has been developed to estimate the pressure drop per foot of packed height, using empirical constants fitted to the data for different types of packing.[14] The formula is as follows:

$$\frac{\Delta P}{Z} = m(10^{-8})(10^{\eta L'/\rho_L})\frac{G'^2}{\rho_G}$$

where:

ΔP = Pressure drop in packed tower

Z = Packed height of tower, in feet

m and n = Pressure-drop constants

L' = Superficial mass liquid velocity lb/hr-ft^2

G' = Superficial mass gas velocity, lb/hr-ft^2

ρ_L = Liquid density, lb/ft^3

ρ_G = Gas density, lb/ft^3

Constants for the above factors are given in Table 3-4.

3.5 CONDENSATION

3.5.1 Introduction

Condensation and subsequent removal of organic compounds is a proved method of reducing organic emission. Many organic compounds, because of their relatively high boiling points, readily condense even though they are not highly concentrated. Thus at a given temperature, if the partial pressure of a compound is increased until it is equal to or greater than its vapor pressure at that temperature, the compound will condense. Alternatively, if the temperature of a gaseous mixture is reduced to the saturation temperature, at which the vapor pressure equals the partial

Table 3–3. CONSTANTS FOR USE IN DETERMINING LIQUID-PHASE HEIGHT OF TRANSFER UNITS[a, 14]

Packing	ϕ	η	L' range, lb/hr-ft^2
Raschig rings			
3/8 in.	0.00182	0.46	400 to 15,000
1/2 in.	0.00357	0.35	400 to 15,000
1 in.	0.0100	0.22	400 to 15,000
1-1/2 in.	0.0111	0.22	400 to 15,000
2 in.	0.0125	0.22	400 to 15,000
Berl saddles			
1/2 in.	0.00666	0.28	400 to 15,000
1 in.	0.00588	0.28	400 to 15,000
1-1/2 in.	0.00625	0.28	400 to 15,000
Partition rings			
3 in.	0.0625	0.09	3,000 to 14,000
Spiral rings (stacked staggered)			
3-in. single spiral	0.00909	0.28	400 to 15,000
3-in. triple spiral	0.0116	0.28	3,000 to 14,000
Drip-point grids			
No. 6146	0.0154	0.23	3,500 to 30,000
No. 6295	0.00725	0.31	2,500 to 22,000

[a] Courtesy of McGraw-Hill Book Co.

Table 3–4. PRESSURE DROP CONSTANTS FOR TOWER PACKING [a, 14]

Packing	m	η	L' range, lb/hr-ft^2	P/Z range, lb/ft^2-ft
Raschig rings				
1/2 in.	139.00	0.00720	300 to 8,600	0 to 2.6
3/4 in.	32.90	0.00450	1,800 to 10,800	0 to 2.6
1 in.	32.10	0.00434	360 to 27,000	0 to 2.6
1-1/2 in.	12.08	0.00398	720 to 18,000	0 to 2.6
2 in.	11.13	0.00295	720 to 21,000	0 to 2.6
Berl saddles				
1/2 in.	60.40	0.00340	300 to 14,100	0 to 2.6
3/4 in.	24.10	0.00295	360 to 14,400	0 to 2.6
1 in.	16.01	0.00295	720 to 78,800	0 to 2.6
1-1/2 in.	8.01	0.00225	720 to 21,600	0 to 2.6
Intalox saddles				
1 in.	12.44	0.00277	2,520 to 14,400	0 to 2.6
1-1/2 in.	5.66	0.00225	2,520 to 14,400	0 to 2.6
Drip-point grid				
No. 6146				
Continuous flue	1.045	0.00214	3,000 to 17,000	0 to 0.5
Cross flue	1.218	0.00227	300 to 17,500	0 to 0.5
No. 6295				
Continuous flue	1.088	0.00224	850 to 12,500	0 to 0.5
Cross flue	1.435	0.00167	900 to 12,500	0 to 0.5

[a] Courtesy of McGraw-Hill Book Co.

pressure of one of the constituents, condensation will also occur. Condensation can thus be accomplished in two ways, by decreasing the temperature or by increasing the system pressure. In most air pollution control applications, condensation is effected by decreasing the temperature. Condensation by increasing pressure is possible, but usually not practical.

Condensers have found a wide range of application in the organic chemical industry where their purpose has been to condense concentrated vapors in the primary process, rather than to reduce contaminant emissions. Applied in the primary process, they recover valuable products and reduce the volume of effluent gas.

Control of organic emissions by condensation is limited by the equilibrium partial pressure of the component. As condensation occurs, the partial pressure of the material remaining in the gas phase decreases rapidly, and complete condensation is not possible. For example, even at 32° F, toluene has a vapor pressure of about 6 millimeters of mercury (mm Hg); at atmospheric pressure (760 mm Hg), a gas stream saturated with toluene would still contain about 8000 ppm of that gas. Thus, condensers must usually be followed by a secondary air pollution control system such as an afterburner, which treats the noncondensible gases and achieves a high degree of overall efficiency. For this reason, condensers have not been used as much as afterburners and adsorbers to control organic gas emissions.

3.5.2 Basic Operating Principles and Types of Equipment

Since condensation is usually accomplished by decreasing the temperature of the vapor, a cold surface or a cooling liquid is deployed in the gas stream to induce condensation.

Condensers may be classified into two groups; namely, surface and contact. In a surface condenser, the vapor to be condensed and the cooling medium are separated by a metal wall; in a contact condenser, the vapor and cooling medium are brought into direct contact.

Surface condensers include the common shell-and-tube-type heat exchangers, as shown in Figure 3-16. In these devices, the cooling medium, usually water, flows through the tubes, and vapor condenses on the outside surface. The condensed vapor forms a film on the cool tubes and drains away to storage or disposal. Air-cooled condensers are usually constructed with finned tubes, and the vapor condenses inside the tubes.

Contact condensers cool the vapor by spraying a cold liquid, usually water, directly into the gas stream. The condensed vapor and water mixture are then usually treated and disposed, or they may be recovered. Contact condensers are, in general, less expensive, more flexible, and more efficient in removing organic compounds than surface condensers. Many variations of the contact condenser exist in addition to the spray tower shown in Figure 3-16. These include the steam or water ejector, and barometric condenser in which the condensing vapors create a negative pressure, which serves to induce the flow of additional vapor from the process.

3.5.3 Design Factors and Applications

The main design factors to be considered in condensing organic compounds are the type(s) of compounds and their temperature, volume, concentration, vapor pressure, and specific heat. When a surface condenser is utilized, knowledge of the heat transfer coefficients on both the vapor and liquid sides is also required. The temperature and amount of coolant available are also important considerations.

In the design of a contact condenser, the amount of cooling water to be used is the critical design factor. This may be computed by calculating the heat to be removed from the condensing vapor: Heat in Btu/hour = (pounds of vapor to be condensed per hour) X (latent heat of vaporization) + (heat capacity of the liquid) X (degrees of subcooling required). The amount of heat that must be removed from the noncondensible gases must also be included. The amount of cooling water required is this heat load divided by the allowable difference in water temperature (inlet water temperature - outlet water temperature).

In a contact type of condenser, about 15 pounds of water (1.8 gallons) at 60° F is required to condense 1 pound of steam at 212° F and cool the condensate to 140° F. Dilution and subcooling of the condensate prevents release of volatile compounds.

In a typical cylindrical contact-spray-chamber condenser, contact times on the order of 1 second with a cross-sectional velocity of about 400 to 500 feet per minute have been used. Pressure drops on the order of 1 inch of water are typical of these units. The use of a contact condenser can result in a water pollution problem, a factor that sometimes restricts the use of this type of condenser.

In the design of a surface condenser, the area of heat exchange is the critical factor. This area is computed by the following equation:

$$A = \frac{Q}{UT_m}$$

Where: A=Heat transfer area, ft^2
Q=Heat to be removed, Btu/hr
U=Overall heat transfer coefficient, Btu/hr-ft^2-°F
T_m=Mean temperature difference, °F

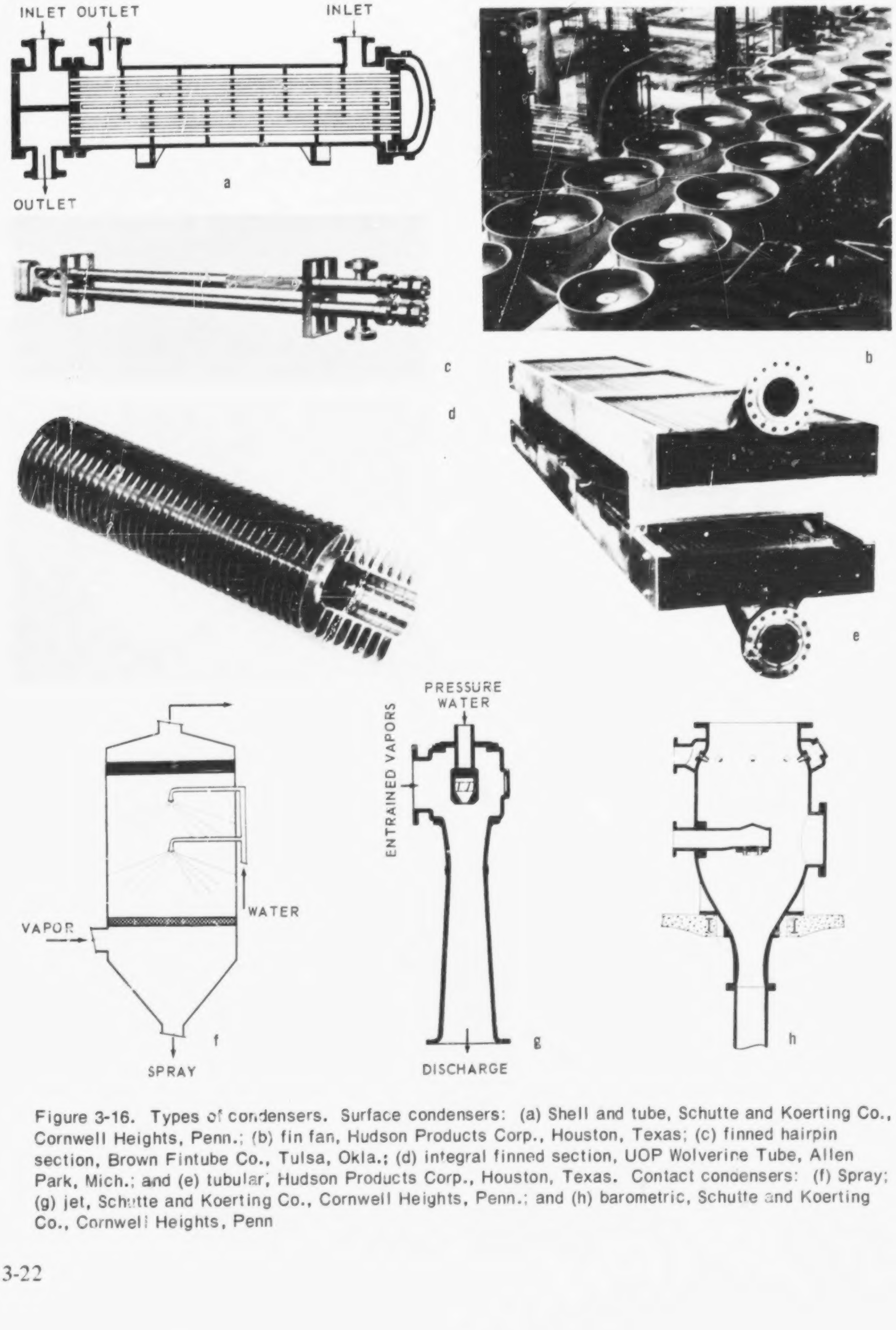

INLET
OUTLET
INLET
OUTLET
a
b
c
d
e
PRESSURE WATER
ENTRAINED VAPORS
WATER
VAPOR
SPRAY
f
DISCHARGE
g
h

Figure 3-16. Types of condensers. Surface condensers: (a) Shell and tube, Schutte and Koerting Co., Cornwell Heights, Penn.; (b) fin fan, Hudson Products Corp., Houston, Texas; (c) finned hairpin section, Brown Fintube Co., Tulsa, Okla.; (d) integral finned section, UOP Wolverine Tube, Allen Park, Mich.; and (e) tubular, Hudson Products Corp., Houston, Texas. Contact condensers: (f) Spray; (g) jet, Schutte and Koerting Co., Cornwell Heights, Penn.; and (h) barometric, Schutte and Koerting Co., Cornwell Heights, Penn

The solution of this equation is difficult since U depends on many parameters of the condensing and cooling streams. A value for U may be estimated by means of a heat balance or may be determined experimentally.[16,17]

Condensers have found a wide range of applications in controlling organic compounds, as shown in Table 3-5. Their application in any specific process depends on the amount and type of coolant available, liquid disposal problems, and the volume of the recovered compounds. Condensers are usually used as preliminary devices and for best control are followed by a more efficient device such as an afterburner or absorber.

3.6 USE OF LESS PHOTOCHEMICALLY REACTIVE MATERIALS

3.6.1 General Considerations

Emission of organic air pollutants from some operations cannot be reduced by the installation of control equipment. For example, solvent evaporation from decorative and protective coatings of buildings and structures cannot be confined for disposal. Industrial surface-coating operations, vapor degreasing, dry cleaning, certain electronic and electrical manufacturing procedures, and some rubber and plastic manufacturing procedures emit organic vapors that *can* be minimized, however, by installing control equipment, but the cost may be prohibitive. An alternative to these "mechanical" techniques for controlling organic emissions from industrial operations is to reformulate the solvent being used so that the emitted material is less reactive.

Photochemical reactivity, or simply "reactivity," is the tendency of an atmospheric system containing the organic compound in question and nitrogen oxides to undergo, under the influence of ultraviolet radiation (sunlight) and appropriate meteorological conditions, a series of chemical reactions that result in the various manifestations associated with photochemical air pollution. These include eye irritation, vegetation damage, and visibility reduction.

All organic compounds, in principle, can be ranked according to their relative ability to undergo photochemical reactions characteristic of smog. For many, however, the data are not available. Furthermore, the ranking of a number of organic compounds on the basis of their rates of disappearnace during photolysis would not necessarily be the same ranking of those same compounds on the basis of their ability to produce eye irritation. Also, these two rankings would be different from the ranking of the same compounds on the basis of their abilities to reduce visibility. A ranking on their ability to cause plant damage would be different still, and so forth. Thus, there are great difficulties in classifying organic compounds according to a photochemical reactivity scale that would be correct for all occasions.[18, 19]

Table 3-5. REPRESENTATIVE APPLICATIONS OF CONDENSERS IN AIR POLLUTION CONTROL

Petroleum refining	Petrochemical manufacturing	Basic chemical	Miscellaneous industries
Gasoline accumulator vents	Polyethylene gas accumulator vents	Ammonia	Drycleaning
Storage vessels	Styrene	Chlorine solutions	Degreasers
Lube oil refining	Copper naphthenates		Tar dipping
	Insecticides		
	Phthalic anhydride		
	Resin reactors		
	Solvent recovery		

3.6.2 Regulations Based on Photochemical Reactivity

In order to regulate organic emissions on the basis of photochemical reactivities, a definition of photochemical reactivity must be adopted. To date, two areas, Los Angeles County and San Francisco Bay Area, have enacted regulations of this type. Both regulations based their definitions of reactivity on the chemical structure of specified materials. The definitions differ because the goals of the two rules differ in degree. The San Francisco Bay Area rule seeks only to limit emissions of very reactive materials, while Los Angeles County's rule also seeks to limit emissions of moderately reactive materials. In order to illustrate this control technique, the principal provisions of both of these rules are given in the following sections. Because the Los Angeles rule was a pioneering effort, some background information leading up to the adoption of the rule is given.

3.6.3 Rule 66 of Los Angeles County

Los Angeles County, which has a severe photochemical air pollution problem, in 1966 enacted a regulation to limit certain organic emissions on the basis of photochemical reactivity. This regulation, entitled Rule 66, applies to organic solvent emissions. Section "k" of this rule[20] defines a photochemically reactive solvent as follows:

> "For the purposes of this rule, a photochemically reactive solvent is any solvent with an aggregate of more than 20 percent of its total volume composed of the chemical compounds classified below or which exceeds any of the following individual percentage composition limitations, referred to the total volume of solvent:
>
> (1) A combination of hydrocarbons, alcohols, aldehydes, esters, ethers, or ketones having an olefinic or cyclo-olefinic type of unsaturation: 5 percent;
>
> (2) A combination of aromatic compounds with eight or more carbon atoms to the molecule except ethylbenzene: 8 percent;
>
> (3) A combination of ethylbenzene, ketones having branched hydrocarbon structures, trichloroethylene, or toluene: 20 percent."

Section "a" limits the emissions from paint baking ovens or heat-curing operations to 15 pounds per day or requires that they be reduced by 85 percent, regardless of the type of solvent used.

Section "b" limits emissions from all other operations using photochemically reactive solvents to 40 pounds per day or requires that they be reduced by 85 percent.

Rule 66.1 prohibits the sale or use of architectural coatings that contain photochemically reactive solvents, as defined above.

Specifically exempt from the provisions of Rule 66"b" are: saturated halogenated hydrocarbons; perchloroethylene; applications of insecticides, pesticides, or herbicides; and the manufacture, transport, or storage of organic solvents.

Rule 66 provides that emission reduction must be accomplished by (1) incineration with at least 90 percent of the carbon in the solvent being oxidized to carbon dioxide, or (2) adsorption, or (3) a method determined to be not less effective than (1) or (2).

The experimental procedures and the evaluation of the results obtained which led up to the provisions of Rule 66 have been described by Hamming.[21]

The control techniques used to secure compliance with Rule 66 have been described by Krenz et al.[22] Some of the methods used are reformulation of the solvents used in the manufacture of paints and other protective coatings, use of direct-fired afterburners to control emissions from paint baking ovens, use of trichloroethane and perchloroethylene in vapor degreasers, and reformulation of petroleum dry-cleaning solvents.

3.6.4 Background of Rule 66

This section was extracted from material prepared by personnel of the Los Angeles

County Air Pollution Control District to explain the need for Rule 66, its scope, history of its development, methodology used in evaluating reactivity of solvents, and implementation of the Rule.

Specific types of hydrocarbons, such as are found in gasoline, had been demonstrated to be active participants in atmospheric reactions responsible for typical smog effects. Additional extensive research by the Los Angeles County Air Pollution Control District has since demonstrated that many organic solvent materials are highly reactive when irradiated in the presence of oxides of nitrogen, and that some of these organic solvents can produce even more ozone and eye irritation than irradiation of auto exhaust. It has also been shown that partial oxidation of solvent vapors prior to their emission to the atmosphere, which occurs in many solvent-using processes, enhances its photochemical reactivity. It is thus apparent that organic solvent emissions contribute significantly to photochemical smog in Los Angeles County.

Several surveys were made to determine the types and quantities of organic solvents used in Los Angeles County. Methods of usage and estimated emissions were obtained from the data obtained.

Preliminary screening of the solvents was accomplished on the basis of eye irritation tests performed by irradiating diluted portions of each solvent in a 50-liter flask.

More extensive tests were performed in larger chambers of 1180-cubic-foot capacity. Solvent vapor concentrations of 2 to 16 ppm were used with 1 or 2 ppm of oxides of nitrogen and irradiation times of 4 to 6 hours. The photochemical reactions were followed by analyzing for hydrocarbons, nitric oxide, nitrogen dioxide, total oxidant, ozone, aldehydes, carbon monoxide, sulfur dioxide, and aerosols.

In evaluating the air pollution potential of a solvent or other test substance, its contribution to any photochemical effect was considered. Such effects include:

1. Eye irritation.
2. Ozone formation.
3. Aerosol formation.
4. Total aldehyde formation.
5. Effect on NO_x reaction.

These criteria were selected as being among the most significant in relation to natural photochemical smog incidents, though not necessarily in the order named. Each solvent or mixture tested was evaluated in terms of these criteria and compared, on the same basis, with auto exhaust in various concentrations, pure olefins, and a "blank" chamber. If a substance being judged equalled or exceeded (the most dilute concentration of) auto exhaust or pure olefins in their ability to produce any of the cited effects, it was considered to be reactive. If it failed to produce any of the cited effects to a degree comparable with that produced by auto exhaust or pure olefins, but greater than that produced by a "blank" or "background" irradiation, it was judged to be nonreactive or inert. Solvents in the "reactive" classification were considered as probably requiring control; those in the "slightly or moderately reactive" classification were regarded as possibly requiring control, but to a lesser extent than those in the "reactive" category; and the "nonreactive" substances were regarded as requiring little or no control.

The efficacy of Rule 66 is attested to by the reduction in the emission of organic solvents since its enactment. By 1969 the emissions of organic solvents would have exceeded a calculated 600 tons per day if uncontrolled. Because of Rule 66, the emission of organic solvents in 1969 not only was reduced to 500 tons per day, but many of the emissions were of the slightly reactive or nonreactive type and, therefore, do not contribute in any great measure to the photochemical smog problem. Future reductions may be confidently expected since it has been demonstrated that compliance with the Los Angeles County solvent control legislation can be achieved by (1) treatment of the organic emissions resulting from solvent usage, (2) converting to less photochemically reactive solvents, or (3) changing the process. An engineering permit system and an enforcement inspection program insure that control equipment to treat the effluent is designed for the required efficiency and operated in compliance with the law.

3.6.5 Applicability of Rule 66 to Other Areas

Rule 66 was designed to alleviate a condition in a specific area. Louis J. Fuller,[23] Air Pollution Control Officer of Los Angeles County, had this to say concerning its applicability to other areas:

> "It has been said that Rule 66 is the most talked about local air pollution legislation in the country. It is true that many communities both from this nation and abroad have inquired about it. I would, therefore, like to caution these communities first to learn the character and extent of their local problems, and then work to resolve them. This rule covers thousands of products, processes, combinations of equipment, production lines, and applications and is framed only for Los Angeles County. It may prove to be unrelated to other areas."

3.6.6 Regulation 3 of San Francisco Bay Area Air Pollution Control District

In 1967, the San Francisco Bay Area Air Pollution Control District adopted a regulation to restrict the emissions of reactive organic materials. Reactive organic compounds are defined as olefins, substituted aromatics, and aldehydes. Not included as olefins are compounds in which all olefinic groups contain three or more halogen atoms. A complying solvent is defined as any organic solvent which emits to the atmosphere organic compounds which on condensation contain 8 percent or less of reactive organic compounds provided that an additional 12 percent of the organic compounds from the emission may be mono-substituted aromatic compounds.[24]

The rule limits organic emissions to 50 ppm, calculated as hexane, unless one of the following requirements is met:

1. A complying material is being used and no heat is applied, or if heat is used and the emission contains fewer than 5 ppm of aldehydes.
2. There are fewer than 5 percent reactives in the organic fraction of the emission.
3. There are fewer than 10 pounds per day reactive organic compounds, or less than 20 pounds per day total organic compounds emitted.
4. The reactive compounds in the emission have been reduced by 85 percent overall.

If heat is applied and the emission contains more than 5 ppm aldehydes, the total organics must be fewer than 50 ppm, or the emission must meet one of requirements 2, 3, or 4 above.

The purpose of this rule is to control the emissions of very reactive compounds only.[25]

3.6.7 Photochemical Reactivity of Trichloroethylene

Los Angeles County Air Pollution Control District, on the basis of studies, divided the common solvents into classes: (1) reactive, (2) slightly or moderately reactive, and (3) nonreactive. Trichloroethylene was placed in category 2.

Stanford Research Institute, under the sponsorship of a group of manufacturers of trichloroethylene, conducted a 2-year smog-chamber study to develop additional data on the photochemical reactivity of trichloroethylene. The summary report of this study, by Katherine W. Wilson,[26] was issued in September 1969. Different experimental conditions and different indices of reactivity from those used in the Los Angeles studies were used in these studies. On the basis of their results, the Stanford group attributed a low photochemical reactivity rating to trichloroethylene.

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4. CONTROL SYSTEMS FOR INDUSTRIAL PROCESSES

Currently, air pollutants can only be controlled at the source. Industrial sources of emissions are controlled by improvement of plant housekeeping or operation, substitution of process or material, and direct prevention of material from escaping to the atmosphere. The process valves in an oil refinery, for example, can be repaired, or furnaces in a mill can be adjusted to give more efficient combustion. A sanitary landfill can be used instead of incineration for disposing of some types of waste materials, or a relatively inert organic solvent can be used to replace a photochemically reactive solvent. Operations that do not directly influence the basic process can sometimes be controlled directly by afterburning, adsorption, absorption, or condensation techniques to prevent the escape of emissions to the atmosphere. At times, the control methods may overlap, or an industry or installation may use more than one of the four basic techniques.

4.1 PETROLEUM REFINERIES

4.1.1 Introduction

From the production of crude oil to the marketing of finished products, the petroleum industry has the potential for emitting significant quantities of hydrocarbon gases and vapors. These emissions are often undesirable; they may also be precursors of photochemical smog. Crude oil is first produced from the ground. Then the liquid hydrocarbons are separated from the gases, light hydrocarbon vapors, and water. Finally, the crude oil is stored until it is removed to the refinery where it is converted to saleable products. In crude oil production, most of the emissions are due to evaporation of hydrocarbons from storage tanks.

The design of a refinery depends on the kind of crude oil it processes and on the final products it manufactures. Refinery operations are most easily discussed, therefore, in terms of their similar functions. Figure 4–1 is a schematic diagram of a typical refining process.

Since crude oil as it is produced has few uses, it is processed to obtain saleable products, such as gasoline, kerosene, fuel oil, petrochemical raw materials, waxes, lubricating oils, and asphalt. Processing involves four major steps: separation, conversion, treatment, and blending.

The first refining step, separation by distillation within a specific temperature range, yields fractions, the relative volumes of which are determined by the nature of the crude oil. These fractions are usually further refined to meet the demands for the various petroleum products. These processes are outlined below:

Conversion by cracking is employed to convert high-molecular-weight hydrocarbons into products of lower molecular weights. For example, cracking partially converts heavy gas oil to gasoline. If a catalyst is used (the more usual case), it is called catalytic cracking; if not, it is thermal cracking. Thermal cracking requires higher temperatures and pressures than those required to catalytic cracking.

Gasoline yield and quality can be improved by several other processes. In catalytic reforming, the molecules of the gasoline feed stock are rearranged and dehydrogenated to produce high-octane gasoline blending stocks. Isomerization rearranges molecules to increase the octane number; it also increases molecular branching, but it does not add to or remove anything from the original material. In still other conversion processes, liquid gasoline is made from the hydrocarbon gases generated during cracking. Polymerization joins two or more olefin molecules. Alkylation joins an

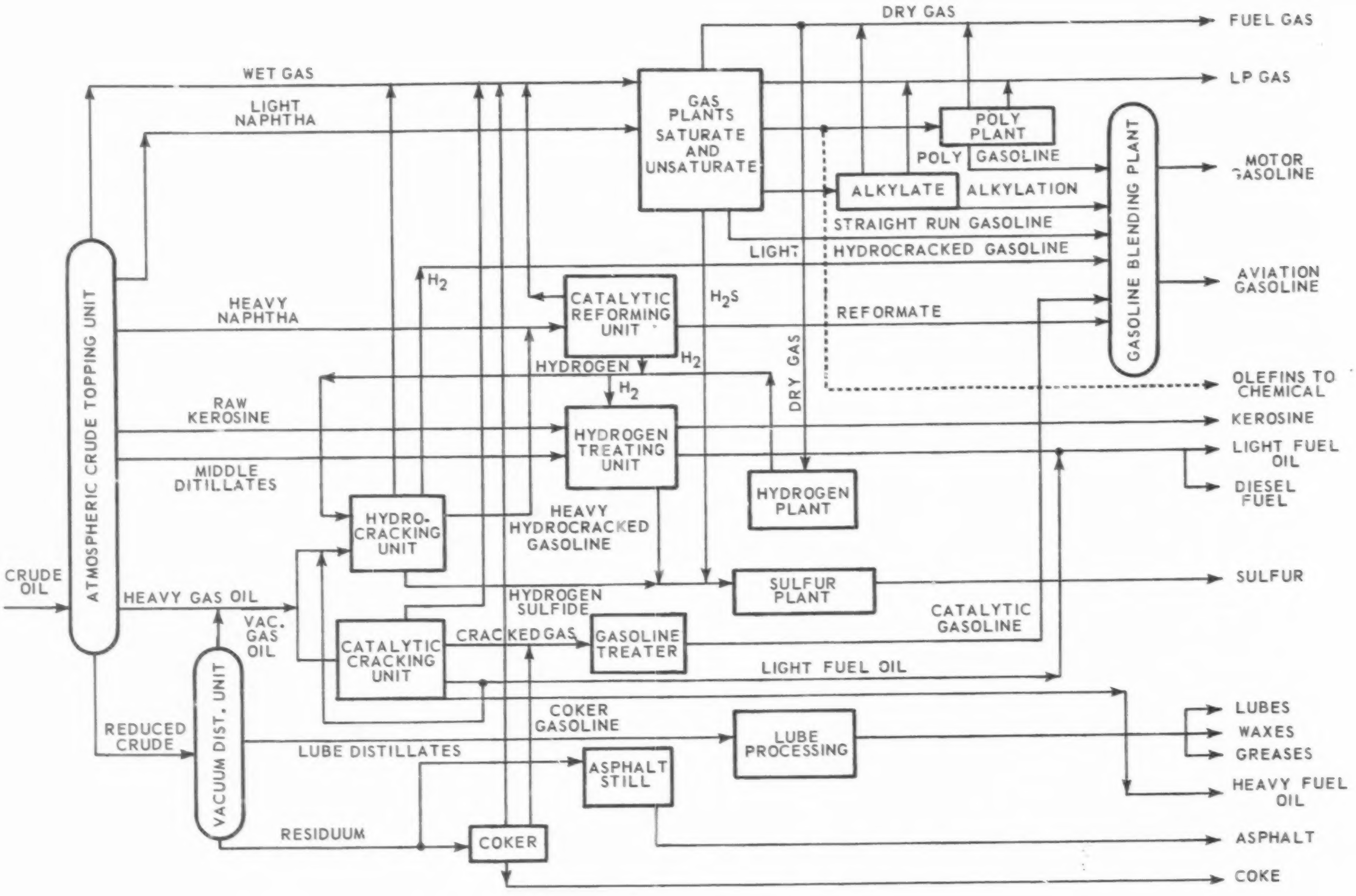

DRY GAS
FUEL GAS
WET GAS
LP GAS
LIGHT NAPHTHA
GAS PLANTS SATURATE AND UNSATURATE
POLY PLANT
POLY
GASOLINE
MOTOR GASOLINE
ALKYLATE
ALKYLATION
STRAIGHT RUN GASOLINE
LIGHT
HYDROCRACKED GASOLINE
GASOLINE BLENDING PLANT
AVIATION GASOLINE
H_2
HEAVY NAPHTHA
CATALYTIC REFORMING UNIT
H_2S
REFORMATE
HYDROGEN
H_2
H_2
DRY GAS
OLEFINS TO CHEMICAL
RAW KEROSINE
HYDROGEN TREATING UNIT
KEROSINE
LIGHT FUEL OIL
MIDDLE DITILLATES
DIESEL FUEL
HYDROGEN PLANT
HYDRO-CRACKING UNIT
HEAVY HYDROCRACKED GASOLINE
ATMOSPHERIC CRUDE TOPPING UNIT
CRUDE OIL
HEAVY GAS OIL
SULFUR PLANT
SULFUR
HYDROGEN SULFIDE
VAC. GAS OIL
CATALYTIC GASOLINE
CATALYTIC CRACKING UNIT
CRACKED GAS
GASOLINE TREATER
LIGHT FUEL OIL
VACUUM DIST. UNIT
COKER GASOLINE
REDUCED CRUDE
LUBE PROCESSING
LUBES
WAXES
GREASES
LUBE DISTILLATES
ASPHALT STILL
HEAVY FUEL OIL
RESIDUUM
COKER
ASPHALT
COKE

Figure 4-1. Processing plan for typical complete refinery[1] (Courtesy of Academic Press, Inc.)

olefin with a branched chain paraffin to yield a saturated hydrocarbon.

Treatment steps are used to purify the material or to prevent an undesirable reaction with an impurity. For example, during selective hydrogenation, sulfur and nitrogen as impurities in the feed stocks are converted to hydrogen sulfide and ammonia, respectively. In addition, olefins and aromatic compounds may be hydrogenated to partial or complete saturation. Three types of treatment employed are acid treatment, "sweetening," and solvent extraction. Petroleum fractions may be brought into contact with concentrated sulfuric acid to remove sulfur, nitrogen, and undesirable unsaturated compounds and to improve color and odor. Sweetening converts mercaptans to disulfides and thus improves odor. Sodium plumbite (doctor), lead sulfide, hyprochlorite, and copper chloride are common sweetening agents. In solvent extraction, solvents are used to remove undesired contaminants or to concentrate desired components.

Physical treatments such as absorption, air-blowing, electrical coalescence, and filtration are used in intermediate refining processes to remove contaminants.

Another commonplace activity at refineries is the blending of base stocks to produce a wide variety of finished products.

A list of equipment, facilities, and processes likely to produce organic emissions in crude oil production and in refining includes:

1. Storage.
2. Catalyst regeneration.
3. Pipeline valves.
4. Pressure relief valves.
5. Pump and compression seals.
6. Loading facilities.
7. Drain and waste separators.
8. Blowdown systems.
9. Boilers and process heaters.
10. Vacuum jets.
11. Chemical treatment.

4.1.2 Storage

Storage is potentially the most important source of hydrocarbon emissions in the petroleum industry. Vapors can be emitted when storage tanks "breathe," when vapors are displaced during filling, and when liquids evaporate. Tanks "breathe" due to the expansion and contraction of their contents with the heat of the day and the cool of the night. When the contents expand, air mixed with hydrocarbon vapors is forced out of the tank. Methods have been developed to estimate losses and to minimize these losses from storage tanks.[2-5]

Pressure tanks, fixed-roof tanks, floating-roof tanks, and conservation tanks provide closed storage. Pressure tanks will withstand pressures exerted by their contents and are themselves a control measure. Fixed-roof tanks are vertical cylinders with a flat, conical, or domed roof; they often have open vents to the atmosphere. Floating-roof tanks have pan, pontoon, or double-deck floating roofs. Pan-floating roofs have flat metal plates for the roofs; they may buckle and lose vapors or sink. In many tanks, pontoon sections have been added to the exposed decks to overcome some of these losses. Center drains can be used to handle the drainage. Pontoon roofs are often used on large-diameter tanks; some have a vapor trap on the underside. Double-deck roofs provide compartmented dead-air space over the entire liquid surface; the bottom deck is often coned upward to trap vapors. Conservation tanks are connected to gas storage systems and have internal flexible diaphragms, or floating plastic blankets.

Floating roofs normally have a sealing element between the roof and tank wall. The floating section is usually about 8 inches smaller in diameter than the tank wall. The space between is usually sealed by vertical shoes (metal plates) connected by braces to the floating roof. The shoes, suspended so that they exert force against the tank wall, are fixed with a suitable fabric between the shoes and the floating roof. The fabric seal extends from the top of the sealing plates to the inner surface of the tank, and its flexibility permits it to seal even riveted areas. A secondary seal can be employed to act as a wiper blade, reducing the wicking action associated with floating roofs. Another type of sealing device is a flexible tube, filled with air or liquid, which rests on the hydrocarbon surface and keeps contact with both the roof and the tank shell. Fixed-roof tanks can often be converted to floating-roof construction by use of commercially available internal elements.

Floating plastic blankets or tiny plastic spheres have been developed to function as floating roofs.[6] These coverings have proved to be effective controls for fixed-roof crude oil tanks. They do not reduce emissions of gasoline or one-component fractions as effectively as the other devices.

A good reflecting paint can reduce evaporation by lowering the temperature of petroleum in storage. Vaporized material can be contained using a vapor-balance system wherein the vapor spaces of all tanks containing the same general classification of products are manifolded together and fed to a reservoir tank from which any excesses can be fed to a flare or a boiler. Vapor recovery systems recover all hydrocarbon vapors, by compression and absorption, as liquid product or as fuel gas.

Tanks may lose vapors at gaging hatches, sample hatches, and relief vents unless these are designed and maintained for proper closure.

4.1.3 Waste-Gas Disposal Systems[7]

Large volumes of hydrocarbon gases are produced in modern refineries and petrochemical plants. Generally, these gases are collected and used as fuel or as raw material for further processing. Sudden or unexpected upsets in process units and scheduled shutdowns, however, can produce gas in excess of the capacity of the gas-recovery system. Emergencies that can cause the sudden venting of excessive amounts of gases and vapors include fires, compressor failures, overpressures in process vessels, line breaks, leaks, and power failures.

A system for disposal of emergency and waste refinery gases normally consists of a manifolded pressure-relieving or blowdown system and a blowdown recovery system, a system of flares for the combustion of the excess gases, or both. In addition to disposing of emergency and excess gas flows, these systems are used in the evacuation of units during shutdowns and turnarounds. Normally, a unit is shut down by depressuring into a fuel gas or vapor recovery system with further depressuring to essentially atmospheric pressure by venting to a low-pressure flare system. Thus, overall emissions of refinery hydrocarbons are substantially reduced.

A blowdown or pressure-relieving system consists of relief valves, safety valves, manual bypass valves, blowdown headers, knockout vessels, and holding tanks. A blowdown recovery system also includes compressors and vapor surge vessels such as gas holders or vapor spheres. Flares are usually considered as part of the blowdown system in a modern refinery.

4.1.3.1 Pressure-Relief Systems

A pressure-relief system can consist of one relief valve, safety valve, or rupture disc or of several relief devices manifolded to a common header. Usually the systems are segregated according to the type of material handled, that is, liquid or vapor, as well as to the operating pressure involved. The following definitions are taken from reference 8:

1. A relief valve is one which automatically opens when the static pressure exceeds a preset value. It opens further with an increase of pressure over the set pressure. It is used primarily for liquid service.
2. A safety valve opens fully when the static pressure exceeds the set pressure. It is used for gas or vapor service.
3. A rupture disc consists of a thin metal diaphragm held between flanges. It is fabricated to rupture at a predetermined pressure.

In a vapor blowdown system a knockout drum is used to remove entrained liquids from the gas stream. This is particularly important if the gas is to be burned in a smokeless flare.

4.1.3.2 Flares[7]

Smokeless flares are of two types, elevated flares and ground-level flares. Flares are elevated in order to safely dissipate the heat released and diffuse any vapors that may be emitted.

Smoke is a by-product of incomplete combustion. Smokeless combustion can be achieved if there is (1) sufficient fuel values in the gas mixture to obtain the minimum theoretical combustion temperature, (2) adequate combustion air, and (3) adequate mixing of the fuel and air.

Smokeless combustion can be obtained in an elevated flare by the injection of an inert gas to the combustion zone to provide turbulence and inspirate air. A mechanical air-mixing system would be ideal, but is not economical in view of the large volume of gases handled. The most commonly used air-inspirating material for an elevated flare is steam. Three main types of steam-injected elevated flares are in use. The difference among them is the manner in which the steam is injected into the combustion zone.

In the first type, steam is injected by several small jets placed concentrically around the flare tip. These jets, installed at an angle, cause the steam to discharge in a converging pattern immediately above the flare tip.

A second type has a flare tip with no obstruction to flow; that is, the flare tip is the same diameter as the stack. The steam is injected by a single nozzle located concentrically within the burner tip. In this type of flare, the steam is premixed with the gas before ignition and discharge.

A third type is equipped with a flare tip constructed to cause the gases to flow through several tangential openings to promote turbulence. A steam ring at the top of the stack has numerous equally spaced holes about 1/8 inch in diameter for injecting steam into the gas stream.

Steam injection is generally believed to result in the following benefits: (1) energy available at relatively low cost can be used to inspirate air and provide turbulence within the flame, (2) steam reacts with the fuel to form oxygenated compounds that burn readily at relatively low temperatures, (3) water-gas reactions also occur with this same end result, and (4) steam reduces the partial pressure of the fuel and retards polymerization.

The injection of steam into a flare can be controlled either manually or automatically. In some installations, the steam is supplied at maximum rates, and manual throttling of a steam valve is required for adjusting the steam flow to the particular gas flow rate. For best combustion at the minimum steam consumption, instrumentation should be provided to automatically proportion the steam rate to the rate of gas flow. A pressure-sensing element located in the gas line as a control system actuates a control valve in the steam supply line. A small bypass valve is usually used to permit a small, continuous flow of steam to keep the steam holes open and permit smokeless burning of small gas flows.

Ground-level flares are of four principal types: horizontal venturi, water injection, multijet, and vertical venturi.

A horizontal venturi-type flare system utilizes groups of standard venturi burners. In this type of burner, the gas pressure inspirates combustion air for smokeless operation.

A water-injection flare consists of a single burner with a water spray ring around the burner nozzle. The water spray inspirates air and provides water vapor for the smokeless combustion of gases. Water is not as effective as steam for controlling smoke with high gas-flow rates, unsaturated materials, or wet gases.

A multijet ground flare uses two sets of burners, one for normal gas release rates and both for higher flaring rates.

A vertical, venturi-type ground flare also uses commercial-type venturi burners. This type of flare is suitable for relatively small flows of gas at a constant rate.

4.1.4 Oil-Water Effluent Systems

A typical waste-water gathering system for a modern refinery usually includes gathering lines, drain seals, junction boxes, and pipes of vitrified clay or concrete for transmitting waste water from processing units to large basins or ponds used as oil-water separators. These basins are sized to receive all effluent water, sometimes even rain runoff; they are constructed as earthen pits, concrete-lined basins, and steel tanks.

Liquid wastes discharging to these systems originate at a wide variety of sources such as pump glands, accumulators, spills, cleanouts, sampling lines, and relief valves.

Organic compounds can escape to the atmosphere from openings in the sewer system, channels, vessels, and oil-water separators. The large exposed surface area of these separators can result in large hydrocarbon emissions to the atmosphere.

The most effective means of control of hydrocarbon emissions from oil-water separators has been the covering of forebays or primary separator sections.[7] Either fixed roofs or floating roofs are acceptable covers. Separation and skimming of over 80 percent of the floatable oil layer takes place in the covered sections. Thus, only a small amount of oil is contained in the effluent water, which flows under concrete curtains to the open afterbays or secondary separator sections.

Satisfactory fixed roofs have been constructed by using wooden beams for structural support and asbestos paper as a cover. A mastic-type sealing compound is then used to seal all joints and cracks. Although this form of roof is acceptable for the control of pollutants, in practice a completely vaportight roof is difficult to achieve. The resultant leakage of air into the vapor space, and vapor leakage into the atmosphere are not desirable from standpoints of air pollution or safety.

The explosion hazard associated with fixed roofs is not present in a floating-roof installation. These roofs are similar to those developed for storage tanks. The floating covers are built to fit into bays with about 1 inch of clearance around the perimeter. Fabric or rubber may be used to seal the gap between the roof edge and the container wall. The roofs are fitted with access manholes, skimmers, gage hatches, and supporting legs. In operation, skimmed oil flows through lines from the skimmers to a covered tank (floating roof or connected to vapor recovery) or sump and then is pumped to demulsifying processing facilities. Effluent water from the oil-water separator is handled in the manner described previously.

In addition to covering the separator, open sewer lines that may carry volatile products can be converted to closed, underground lines with water-seal-type vents. Junction boxes can also be vented to vapor recovery facilities, and steam can be used to blanket the sewer lines to inhibit formation of explosive mixtures.

4.1.5 Cracking Catalyst Regeneration

Petroleum fractions are cracked to produce compounds of lower molecular weight. Catalysts in the form of powders or beads are utilized. The catalyst particles become coated with carbon and high-molecular-weight compounds. These materials must be burned off the catalyst in order to maintain its activity. The catalyst continuously circulates from the reactor chamber to the regenerator chamber. In the regenerator, a controlled amount of air is admitted to burn off the coatings. This causes the formation of CO and hydrocarbons. These emissions can be controlled by incineration using a waste heat boiler. These boilers are commonly referred to as CO boilers.[7]

4.1.6 Pumps

Pumps are used in every phase of the petroleum industry. Leakage from pumps can cause organic emissions wherever organic liquids are handled. The opening in the cylinder or fluid end through which the connecting rod actuates the piston is the major potential source of emissions from a reciprocating pump. In centrifugal pumps, the usual source of leakage is the point at which the drive shaft passes through the impeller casing.

Several means have been devised for sealing the annular clearance between pump shafts and fluid casings to retard leakage. For most refinery applications, packed seals and mechanical seals are widely used.

Packed seals can be used on both positive-displacement and centrifugal-type pumps. Typical packed seals generally consist of a stuffing box filled with sealing material that encases the moving shaft. The stuffing box is fitted with a takeup ring which is made to compress the packing and cause it to tighten around the shaft. Materials commonly used for packing are metal, rubber, leather, wood, and plastics.

The contact surfaces of the packing and shaft are lubricated by a controlled amount of product leakage to the atmosphere. This feature makes packing seals undesirable in applications where the product can cause a pollution problem. The packing may also be saturated with some material such as graphite or oil that acts as a lubricant.

The second commonly used means of sealing is the mechanical seal. This type of seal can be used only in pumps that have a rotary shaft motion. A simple mechanical seal consists of two rings with wearing surfaces at right angles to the shaft. One ring is stationary while the other is attached to the shaft and rotates with it. A spring and the action of fluid pressure keep the two faces in contact. The wearing faces are lubricated by a thin film of the material being pumped. The wearing faces, usually made of carbon, are precisely finished to insure perfectly flat surfaces.

Emissions to the atmosphere from centrifugal-type pumps may be controlled in some cases by use of the described mechanical-type seals instead of packing glands. For cases that cannot be controlled with mechanical seals, special pumps, such as canned or diaphragm pumps, are required.

The canned pump is totally enclosed, with its motor built as an integral part of the pump. Seals and attendant leakage are eliminated. The diaphragm pump is another type devoid of seals. It has no moving parts except a flexible diaphragm whose back-and-forth motion coupled with intake and discharge valves effects a pumping action.

Other than the direct methods used to control leakage, operational changes may minimize release of emissions to the atmosphere. One desirable change is to bleed off pump casings during shutdown to the fuel gas system, vapor recovery facilities, or a flare instead of directly to the atmosphere.

4.1.7 Air-blowing of Asphalt

Asphalt is normally obtained from select crude oils by means of vacuum distillation or solvent extraction. To make it suitable for paving, roofing, or pipe coating, asphalt is sometimes reacted with air. Air-blowing is mainly a dehydrogenation process. Oxygen in the air combines with hydrogen in the oil molecules to form water vapor. The progressive loss of hydrogen results in polymerization or condensation of the asphalt to the desired consistency.

Blowing is usually carried out in batches, starting with the asphalt at a temperature of 300° to 400°F. Little additional heat is needed since the reaction becomes exothermic.

Effluents from the asphalt air-blowing stills include oxygen, nitrogen, water vapor, sulfur compounds, and hydrocarbons in the forms of gases, odors, and aerosols. Discharge of these odors and airborne oil particles can be disagreeable.

Control of emissions from asphalt air-blowing stills has been accomplished by scrubbing and incineration, singly or in combination.[7] Most installations use the combination. For scrubbing alone to be effective, a very high water-to-gas ratio of about 100 gallons per 1,000 standard cubic feet per minute is necessary.

Where removal of most of the potential air pollutants is not feasible by scrubbing alone, the noncondensibles must be incinerated. Essential to effective incineration is direct-flame contact with the effluents, a minimum retention time of 0.3 second in the combustion zone, and maintenance of a minimum combustion chamber temperature of 1,200°F. Other desirable features include turbulent mixing of vapors in the combustion chamber, and adequate instrumentation. Primary condensation of steam and water vapor allows use of smaller incinerators and results in fuel savings. Some of the heat released by incineration of the waste gases may be recovered by using it to generate steam.

4.1.8 Valves

Valves are employed in every phase of the petroleum industry where petroleum or petroleum products are transferred by piping from one point to another. Pressure relief valves are discussed in Section 4.1.3.1.

Manual and automatic flow control valves are used to regulate the flow of fluids through a system. These valves are subject to product leakage from the valve stem as a result of the actions of vibration, heat, pressure, and corrosion or improper maintenance of valve stem packing.

Obviously, the controlling factor in preventing leakage from valves is maintenance. An effective schedule of inspection and preventive maintenance can keep leakage at a minimum. Minor leaks that might not be detected by casual observation can be located and eliminated by thorough periodic inspections.

4.1.9 Loading Facilities

Losses from refinery loading facilities can be handled similarly to losses from distribution facilities, as discussed in Section 4.2.

4.1.10 Vacuum Jets

Emissions of hydrocarbons from vacuum jets can be controlled by venting the discharge to blowdown or vapor-recovery systems. These hydrocarbon emissions may also be vented to the firebox of a boiler or heater.

4.1.11 Boilers and Process Heaters

Proper maintenance of burner equipment is essential to proper control of boilers and process heaters to assure efficiency of combustion and minimum emission of unburned hydrocarbons. Choice of fuel is important in some types of equipment, which may be designed for preferential use of gas, oil, or solid fuels. In many types of fireboxes, however, provision is made for manual or automatic switching from one fuel to another or from the simultaneous burning of different fuels. Close attention to the operation of the equipment is important in maintaining optimum burning conditions.

4.1.12 Chemical Treating Processes

In acid treatment, emissions can be reduced by substituting continuous mechanical mixing for batch-type agitators that employ air-blowing for mixing. Acid regeneration can also be used instead of the hydrolysis-concentration method of acid recovery. Gases emitted during acid-sludge recovery can be vented to caustic scrubbers to remove sulfur dioxide and odorants. Gases from scrubbers can then be vented to a firebox or flare. For new installations, acid treatment can also be replaced by catalytic hydrogenation or by other processing techniques that may prove to be more effective.

In doctor treating, the doctor solution can be steam-stripped to recover hydrocarbons prior to air-blowing for regeneration. The effluent from air-blowing can then be incinerated to destroy hydrocarbon vapors.

In the disposal of spent caustic, entrained hydrocarbons are often removed by stripping with inert gases. The vapors removed in this stripping operation can be vented to a flare or to a furnace firebox.

Whenever hydrocarbons are removed in air- or gas-blowing operations, the effluent hydrocarbons can be destroyed by incineration.

4.2 GASOLINE DISTRIBUTION SYSTEMS

4.2.1 Introduction

Gasoline and other petroleum products are distributed from the refinery to the consumer by pipelines, trucks and trailers, railroad tankcars, and ocean-going tankers, all of which form a distribution network, as shown in Figure 4–2. Intermediate storage and loading stations that receive products from refineries by pipeline or tanker are called terminals;

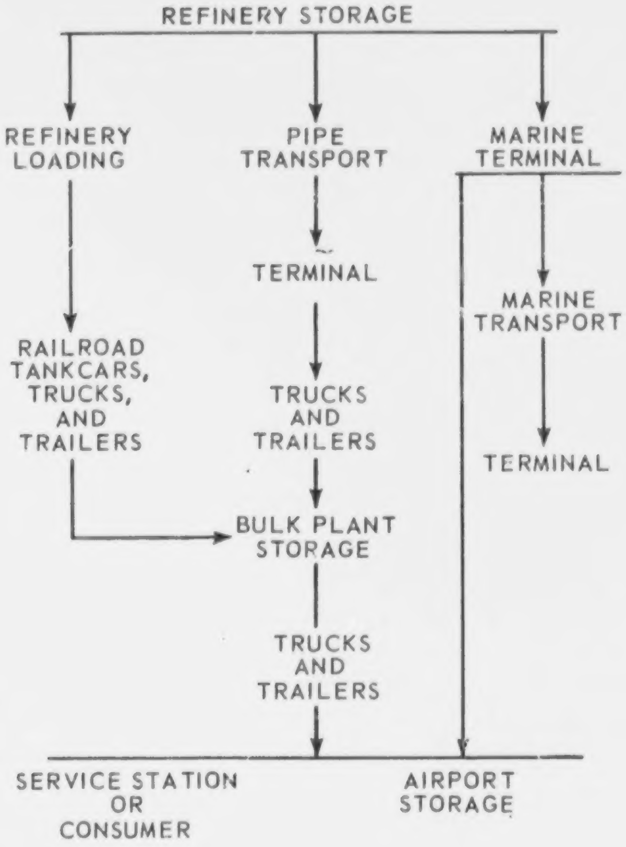

REFINERY STORAGE
REFINERY LOADING
PIPE TRANSPORT
MARINE TERMINAL
TERMINAL
MARINE TRANSPORT
RAILROAD TANKCARS, TRUCKS, AND TRAILERS
TRUCKS AND TRAILERS
TERMINAL
BULK PLANT STORAGE
TRUCKS AND TRAILERS
SERVICE STATION OR CONSUMER
AIRPORT STORAGE

Figure 4-2. Representation of gasoline distribution system, showing flow of gasoline and other petroleum products from refinery to consumer.

those supplied by trucks and trailers are called bulk plants.

Marine terminals are bulk storage installations adjacent to docks; petroleum products are stored in them prior to being loaded into ocean-going tankers. Petroleum products are loaded into trucks, trailers, and tankcars at bulk installations by means of loading racks. These racks contain equipment to meter and deliver the various products into vehicles from storage.

4.2.2 Emissions

When a tank truck or tanker is filled through an open overhead hatch or a bottom connection, the incoming liquid displaces the contained vapors. The displaced vapors, which are forced out into the atmosphere, usually consist of a mixture of air and hydrocarbons. Ordinarily, when gasoline is loaded, the hydrocarbon concentration of the vapors is 30 to 50 percent by volume and the hydrocarbons consist of gasoline fractions ranging from propane through hexane. Table 4-1 shows a typical analysis of the vapors emitted during the loading of motor gasoline into tank vehicles.[9]

The volume of vapors produced during loading operations, as well as the composition, is greatly influenced by the type of loading or filling employed.[9] Overhead loading, presently the most widely used, may be further divided into splash and submerged filling. In splash filling, the outlet of the delivery tube is above the liquid surface during all or most of the loading. In submerged filling, the outlet of the delivery tube is extended to

Table 4-1. TYPICAL ANALYSIS OF VAPORS FROM LOADING OF GASOLINE INTO TANK TRUCKS

Fraction	Volume, %	Weight, %
Air	58.1	37.6
Hydrocarbon	41.9	62.4
Propane	0.6	0.6
Iso-butane	2.9	3.8
Butene	3.2	4.0
N-butane	17.4	22.5
Iso-pentene	7.7	12.4
Pentene	5.1	8.0
N-pentane	2.0	3.1
Hexane	3.0	8.0

within 6 inches of the bottom and is submerged beneath the liquid during most of the loading. Bottom loading is accomplished by connecting a swing-type loading arm or hose at ground level to a matching fitting on the underside of the tank vehicles (Figure 4–3). Splash filling generates more turbulence and therefore more hydrocarbon vapors than submerged filling. In bottom loading, all the loading is submerged, thus turbulence is minimized and less vapor is produced.

Loading and unloading operations are the primary sources of emissions in the distribution of gasoline and petroleum products.

4.2.3 Controls

To control vapor emission from loading operations, devices can be installed to collect the vapors at the tank vehicle hatch.

4.2.3.1 Overhead Loading

Four types of vapor collectors have been developed for use during overhead loading operations. All are essentially plug-shaped devices that are inserted into a fitting for the hatch opening. Gasoline flows through a central channel in the device into the tank vehicle compartment. This central channel is surrounded by an annular space into which vapors enter through openings on the bottom of the hatch fitting. The annular space is in turn connected to a hose or pipe leading to a vapor disposal system.

The Mobile Oil Corporation device, shown in Figure 4–4, is connected to a vapor chamber with a transparent section to allow the operator to see the calibrated capacity markers located within the tank compartment. This closure has adjustable height. It requires a constant downward force to keep it firmly in place during filling. It is built to fit only hatches 8 to 10 inches in diameter.

The Chiksan device in Figure 4–5 incorporates the hatch closure, the vapor return line,

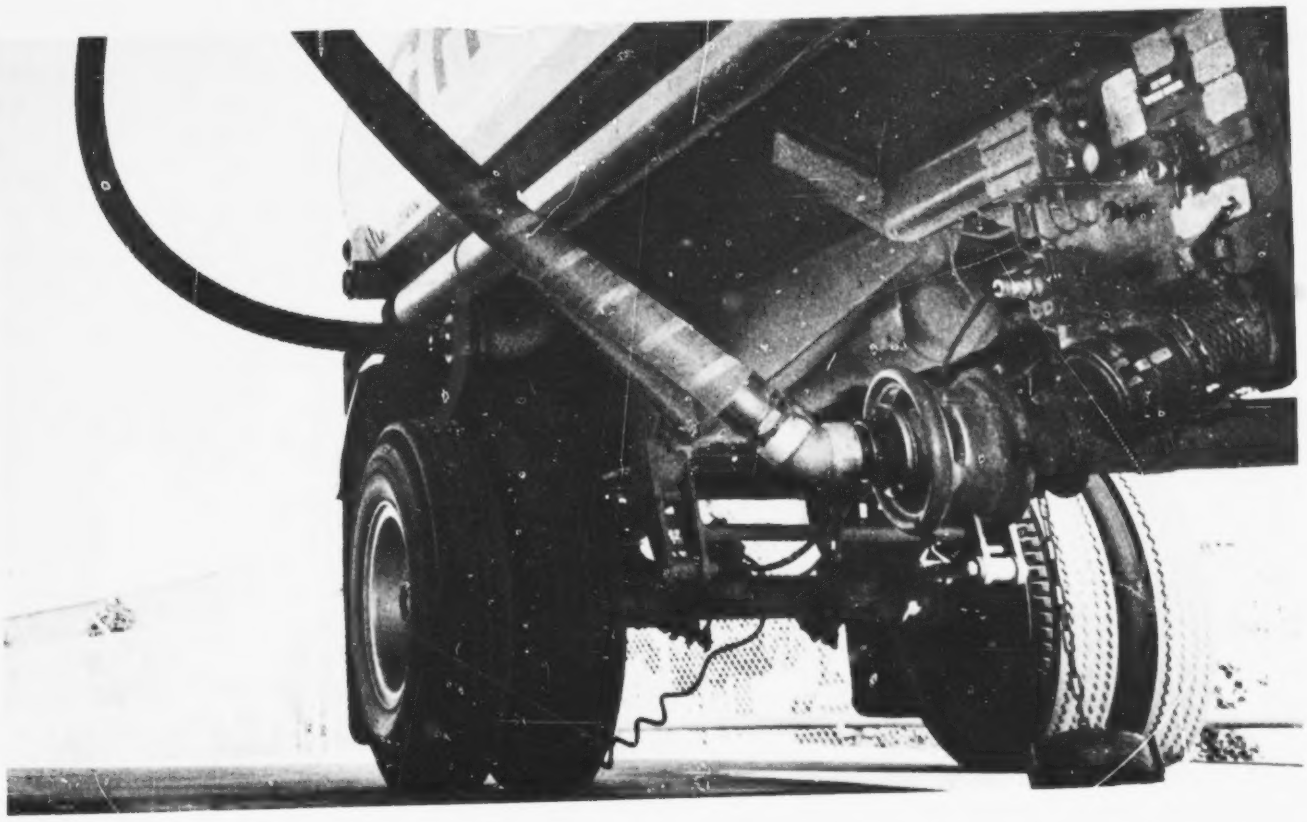


Figure 4-3. View of bottom-loading station. (Courtesy Standard Oil Company of California, Western Operations, Inc., San Francisco, Cal.)

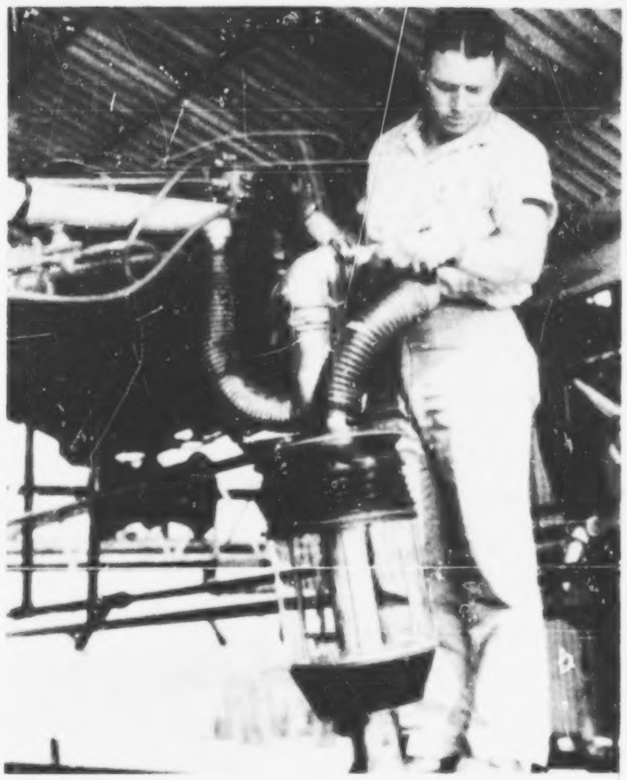


Figure 4-4. View of Mobil Oil Corporation vapor closure.

(Courtesy of Mobil Oil Corporation, Los Angeles, Cal.)

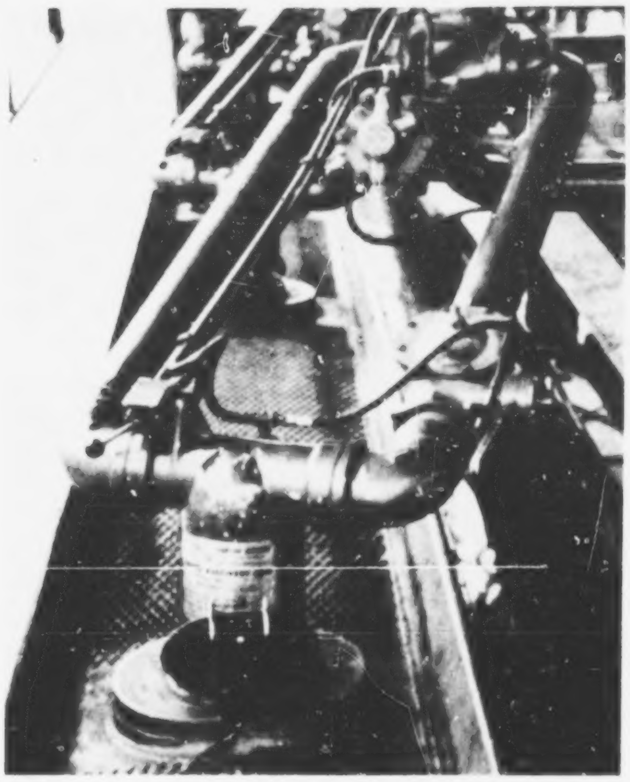


Figure 4-5. Chiksan pneumatically operated loading assembly with integrated vapor closure and return line.

(Courtesy of Chiksan Co., Brea, Cal.)

and the fill line into an assembled unit. This unit has features to prevent overfills, topping off, or filling unless the assembly is properly seated in the tank hatch.

The Greenwood vapor closure, shown in Figure 4–6, developed by the Vernon Tool Company, also requires downward force during filling. It ordinarily does not have a transparent vapor chamber. This closure has an adapter for hatches larger than 10 inches.

Developed by the Standard Oil Company of California, the device shown in Figure 4–7 has a positive clamp for the hatch opening, which, when closed automatically actuates the vapor chamber. It also has a safety shutoff float that senses the gas level and prevents overfilling. These SOCO devices can be used with adapters for hatches larger than 8 inches in diameter.

The slide positioner of the Mobile Oil Corporation device can be a source of vapor leaks and requires close attention by the operator during adjustments for fitting and submerged loading. The inner valves of the SOCO devices make them considerably heavier than other types. This device increases pressure drop and slows the loading rates. Mobil and Greenwood devices both require check valves in the vapor-gathering lines to prevent the vapor from discharging back to the atmosphere when the assembly is withdrawn. In addition, these devices require nearly vertical entry of the loading tube into the hatch opening in order to provide a tight seal against vapor leaks. An assembly is available to assure that the Greenwood device maintains this vertical position.

4.2.3.2 Bottom Loading

Bottom loading permits easier collection of displaced vapors. Because the filling line and the vapor collection line are independent of each other, collection during bottom loading is relatively easy. The vapor collection line consists of a flexible hose or swing-type arm connected to a quick-acting valve fitting on the dome of the vehicle. A check valve must, of course, be installed on the vapor collection

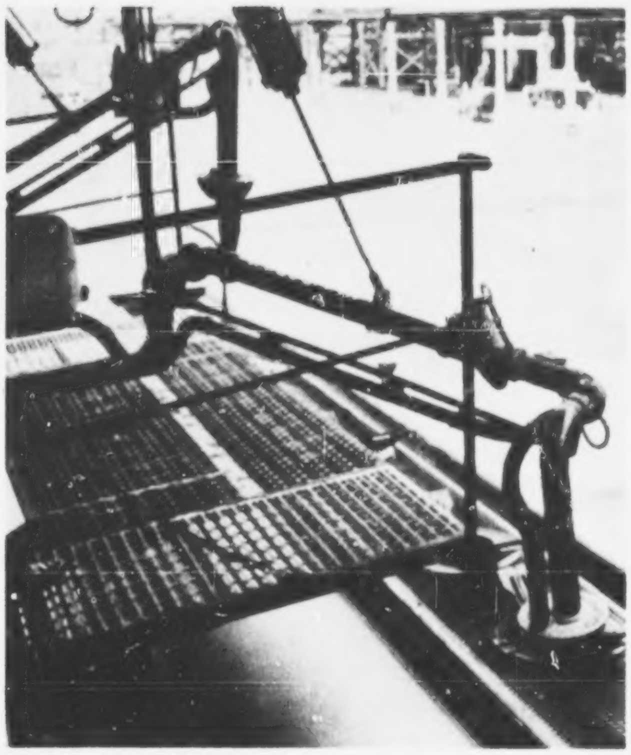


Figure 4-6. View of Greenwood vapor closure.
(Courtesy of Atlantic-Richfield Oil Corporation, Los Angeles, Cal.)

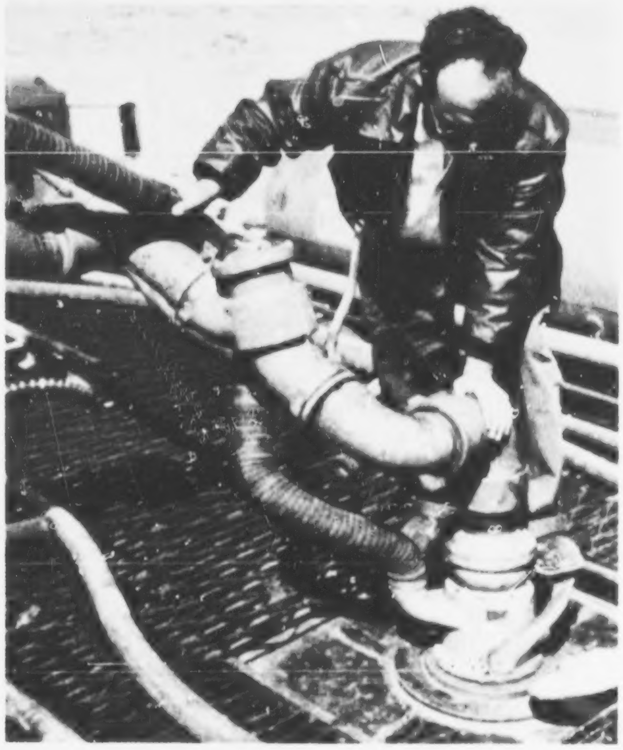


Figure 4-7. SOCO vapor closure device in filling position.
(Courtesy of American Airlines, Los Angeles, Cal.)

line to prevent backflow of vapors to the atmosphere when the connection to the tank is broken.

4.2.3.3 Vapor Disposal

Vapors collected during loading operations may be used as fuel or may be recovered as a product. When fired heaters or boilers are available, the displaced vapors may be directed through a drip pot to a small vapor holder, which is gas-blanketed to prevent formation of explosive mixtures. The vapors are drawn from this holder by a compressor and discharged to the fuel gas system.

If the loading facility is near the refinery, the vapor line can be connected from the loading facility to an existing vapor recovery system through a regulator valve. If not, packaged units may be used to recover vapors. Figure 4–8 shows an absorption unit developed by the Superior Tank and Construction Company. It includes a tank equipped with a flexible membrane diaphragm, a saturator, an absorber, compressors, pumps, and instruments. These units use the gasoline product as the absorbent. In operation, these units avoid the accumulation of explosive mixtures by passing the vapors displaced at the loading rack through a saturator countercurrently to gasoline pumped from storage. The saturated vapors then flow to the vaporsphere, where a diaphragm controls a compressor, which draws the vapors from the sphere and injects them at about 200 pounds per square inch (guage) into the absorber. Gasoline used to absorb the hydrocarbon vapors is returned to storage, while the remaining gases, mostly air, are released to the atmosphere through a back-pressure regulator. Some difficulty has been experienced with air entrained in the gasoline returning to storage. Any such air released in the storage tank is saturated with hydrocarbon vapors as it is discharged. This air can be properly removed by flashing the liquid gasoline from the absorbed in one or more additional vessels operating at successively lower pressures.

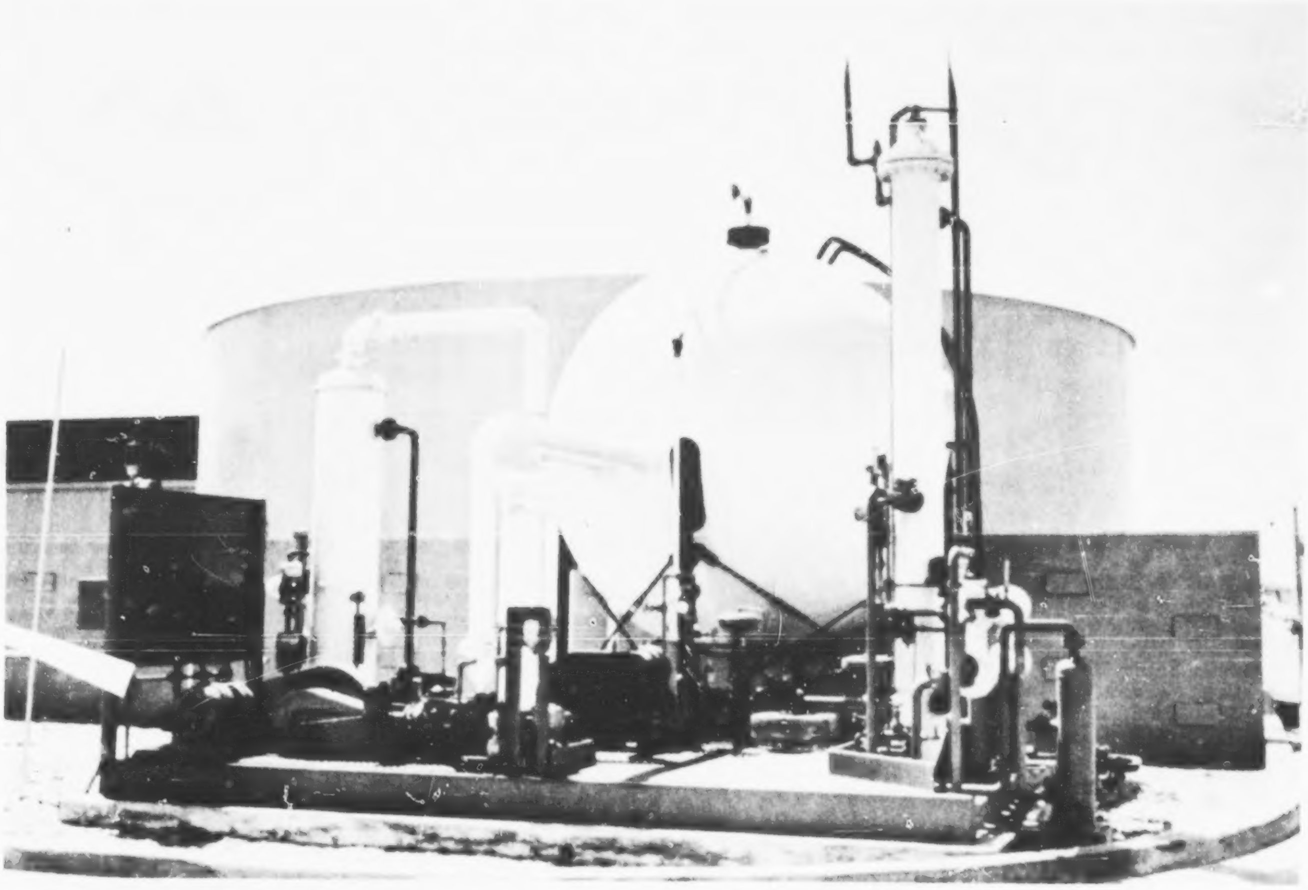


Figure 4-8. Small-capacity vaporsaver gasoline absorption unit.
(Courtesy of American Airlines, Los Angeles, Cal.)

4.2.4 Regulations and Costs

Regulations pertaining to gasoline loading systems have been applied primarily in Los Angeles County, where about 8 percent of the total petroleum refining capacity of the United States is concentrated. Rule 61, adopted in 1956, requires control on large bulk-gasoline loading installations. Compliance with this rule by the industry has resulted in an estimated reduction of hydrocarbon emissions of about 50 tons daily in Los Angeles County.[10] Emissions from bulk loading without controls would be about 145 tons per day.

These controls represent investments of more than $3 million by the petroleum industry, and payouts are estimated at 30 months to 5 years. Besides recovery of products in some of the control systems, other benefits have resulted, such as better working conditions for operating personnel. Gasoline losses from spills, overfills, and loading arm drainage have also been minimized.

The cost of a bulk storage control system in 1968 was proportional to the gasoline throughput. A system consisting of loading arms, a vapor holding tank, and a Vaporsaver unit for absorption, costs approximately $90,000 for a terminal with a throughput of somewhat less than 300,000 gallons per day, and approximately $125,000 for a terminal with a throughput of 750,000 gallons per day.

4.3 CHEMICAL PLANTS

4.3.1 Introduction

Manufacturers of synthetic organic chemicals such as elastomers, dyes, flavors, perfumes, plastics, resins, plasticizers, pigments, pesticides, rubber processing chemicals, and miscellaneous solvents have the problems of controlling emissions of hydrocarbons from raw materials and from products made from these materials. According to the U.S. Tariff Commission, 3,092 million gallons of raw materials was consumed by the chemical industry in 1967.[11] These raw materials were obtained from coal (coke oven gas, coal tar, water-gas, and oil-gas tar) and from petroleum. The quantities of the most important raw materials–benzene, toluene, xylene, naphthalene, and creosote oil–are shown in Table 4–2. The total of crude products produced from petroleum and natural gas amounted to 54,436 million pounds in 1967, an increase of 8 percent over 1966. The quantity of each product is itemized in Table 4–2. From these crude products, a total of 80,256 million pounds of synthetic organic chemicals was produced, as itemized in the same table.

4.3.2 Processes

Organic chemicals, or petrochemicals, are largely manufactured by conversion processes. Many of the conversions involve complicated reactions; most involve (1) continuous processing in large volume and (2) control by

Table 4–2. QUANTITIES OF RAW MATERIALS AND INTERMEDIATE PRODUCTS CONVERTED TO SYNTHETIC ORGANIC CHEMICALS IN 1967

Raw materials produced from coal[a] and petroleum		Quantity, 1000 gal.
Benzene	90,642	878,704
Toluene	19,357	624,454
Xylene	5,488	449,349
Naphthalene	520,991	376,679
Creosote Oil	126,234	- - -
Total	762,712	2,329,186
Crude products produced from natural gas and petroleum		Quantity, 1000 gal.
C_2 hydrocarbons:	acetylene	16,455
	ethane	429
	ethylene	1,557
C_3 hydrocarbons:	propane	11,855
	propylene	4,123
	propane-propylene	5,771
C_4 hydrocarbons		617
C_5 hydrocarbons		8,227
All other aliphatics and derivatives		784
Aromatics and naphthenes		4,618
Total		54,436
Synthetic organic chemical produced		Quantity, 1000 gal.
Miscellaneous chemicals and solvents		59,695
Dyes		206
Elastomers		3,822
Flavor and perfume materials		112
Pesticides and related products		1,049
Pigments		53
Placticizers		1,262
Plastics and resins		13,793
Rubber processing chemicals		264
Total		80,256

[a] The U.S. Tariff Commission figures for coal are for coke oven gas, coal, water gas, and oil-gas tar.

automated instrumentation. Many are systems-controlled through computers. Generally, the type of emission is identified by the type of raw material and auxiliary raw material, and the type of conversion.

Pipelines, barges, and ships, by facilitating the delivery of raw materials and products, have provided fundamental stimulation of the growth and geographic spread of petrochemical manufacturing.

Of the thousands of chemical manufacturing processes, each has unique control problems. The types of chemical conversions utilized in these processes are classified below.

Alkylation is the union of an olefin with an aromatic or paraffinic hydrocarbon. Ethyl benzene is produced by alkylating benzene with ethylene,[12] and naphthalene, by dealkylation of a petroleum fraction.[13]

In amination, an amino compound is formed by using ammonia (or a substituted ammonia) as the agent. Other amines are made by reducing a nitro compound. Ethanolamines, for example, are obtained when ethylene oxide is bubbled through an ammonia solution.

Hydrogenation, the addition of hydrogen, is used to manufacture a broad range of products. For example, methanol is made by reacting CO with hydrogen.

Dehydrogenation, the removal of hydrogen, produces unsaturated compounds. Benzene is made by dehydrogenation of substituted cyclohexanes.

Dehydration, the removal of water, produces ethers from alcohols. Hydration, the addition of water, produces ethyl alcohol from ethylene.

In esterification, an alcohol reacts with an organic acid to form an ester. Ethyl alcohol reacts with acetic acid to form ethyl acetate, an important solvent.

Halogenation and dehalogenation are the addition or removal of a halogen. Methyl chloride is made by chlorination of methane. Chlorine, bromine, iodine, and fluorine are the halogenation agents.

Oxidation, the addition of oxygen, is one of the most valuable conversion processes. Ethylene oxide is made by oxidation of ethylene. The cheapest oxidizing agent is air, but pure oxygen has advantages in many applications.

Nitration introduces nitrogen into hydrocarbons. Nitrobenzene is an important product of nitration.

Polymerization is the reaction of simple molecules to form more complex polymers. For example, ethylene is polymerized to polyethylene.

The raw materials and the products are potential sources of emissions in any chemical conversion operation. Chemical reactions for production of a desired product usually result in several by-products. Although the formation of by-products is minimized by adjusting the conversion conditions, the quantities formed must be either recovered for use or be properly disposed of as wastes. Waste disposal is a primary problem, complicated by the fact that wastes may be highly toxic. Thus air-cleaning methods that merely transfer the emissions to streams or other waters are not satisfactory.

The major sources of emissions to the air are streams of waste gases, vapors from distillation columns, and leakage from feed and product transport lines. Many chemical plants generate their own steam for use in refining and for supplying power; therefore, emissions characteristic of power plants are an inherent part of the total. The manufacture or regeneration of catalysts usually results in nonhydrocarbon emissions.

Many plants that produce their own crude products have emissions similar to those from petroleum plants. Annual total emissions were estimated for a plant producing 500 million pounds per year of ethylene. Emission factors, taken from Public Health Service Publication No. 763,[14] were used for individual pieces of equipment, to derive the results shown in Table 4–3. For these estimates, all pumps, compressors, valves, etc., were counted and the composition of the process streams were delineated.

Table 4–3. CALCULATION OF HYDROCARBON LOSSES FROM PROCESS EQUIPMENT IN 500 MILLION-LB/YR ETHYLENE PLANT[15]

Emission source	Loss factor[a]	Number of capacity	Emissions, lb/day
Valves	0.15 lb/day-valve	4500 valves x 0.15	= 675
Pumps (mech. seal)	3.2 lb/day-seal	150 pumps x 3.2	= 480
Compressors (centrifugal, mechanical seal)	3.2 lb/day-seal	10 comp. x 2 x 3.2	= 64
Compressors (reciprocating, packed seal)	5.4 lb/day-seal	1 comp. x 5.4	= 5
Cooling water	6.0 lb/10^6 gal	$\frac{50{,}000 \text{ gpm} \times 60 \times 24 \times 6}{1{,}000{,}000}$	= 430
Process drains and waste water separators	150 lb/1000 bbl capacity	$\frac{20{,}000 \text{ bbl} \times 150}{1{,}000}$	=3000
Blowdown systems	100 lb/1000 bbl capacity	$\frac{20{,}000 \text{ bbl} \times 150}{1{,}000}$	=2000
Relief valves (operating vessels)	2.9 lb/day-valve	400 valves x 2.9	=1150
Relief valves (storage tanks)	0.6 lb/day-valve	14 tanks x 2 valves x 0.6	= 17
Storage tanks (floating roof)(VP<1.5 psi)	4.8 lb/day-1000 bbl cap.	$\frac{500{,}000 \text{ bbl} \times 4.8}{1{,}000}$	=2400
Storage tanks (floating roof) (VP>1.5 psi)	1.7 lb/day-1000 bbl cap.	$\frac{5{,}000 \text{ bbl} \times 1.7}{1{,}000}$	= 9
Miscellaneous losses	10 lb/day-100 bbl cap.	$\frac{20{,}000 \text{ bbl} \times 10}{1{,}000}$	= 200
		Total calculated hydrocarbon emission	10,430 lb/day
		Loss on plant feed[b] $\frac{10{,}430}{20{,}000 \times 250}$	= 0.21 wt %

[a] These loss factors are applicable to plants practicing extensive hydrocarbon control.

[b] The range of emissions from hydrocarbon processing plants may range from 0.1 to 0.6% by weight of plant throughout. The lower value calculated here is applicable to an area such as Los Angeles County where stringent control is practiced.

4.3.3 Emission Controls

Often, control of emissions by the chemical industry is based on economic incentives. In other words, condensers are used to recover vapors containing usable reactants, and wastes are burned to recover heat value. Thus, since the prevention of losses is usually considered a part of the process, investment data from contractors include the cost of such conventional controls. Investment data do not, however, ordinarily include controls such as catalytic fume burner systems, thermal incinerators, or special adsorbers required to remove contaminants from exhaust gas streams.

Catalytic oxidations are seldom, if ever, free of odor. Large quantities of air pumped through the reaction system to provide the oxygen necessary for the conversion. Low concentrations of the main reactants are carried into the air. Existing methods for recovery of these low concentrations are often unattractive economically, in the sense that the recovered material does not pay for the cost of recovery. Recently, however, new developments in recovery methods have begun to reduce the economic burden of recovery or disposal and, in some cases, have begun to indicate a profit potential. These are discussed below.

4.3.3.1 Collection of Vented Gases

Frequently, waste gases from columns, partial condensers, or other equipment pollute air or produce smog when they are vented to the atmosphere. It is not profitable to use conventional reciprocating or centrifugal compressors to collect these streams for incineration. In addition, some waste gases with a low heating value may not give the desired heat release because of inert materials present. This problem can be overcome by using automated jet-compressors, which use a good fuel as the motive gas and can be operated to give good combustible exhausts.[16] The automated jet-compressor is a special type of jet ejector, made of five basic parts as shown in Figure 4-9. First, the secondary or waste gases enter body A where they are entrained by high-pressure motive gases from nozzle B; then this mixture is discharged at an intermediate pressure from diffuser C. Spindle operator D can move spindle E to vary the motive gas rates so that the required pneumatic relationships are maintained. The device can operate at constant suction pressure, constant discharge pressure, or constant ratio of motive gas to waste gas. The gases can be discharged directly to a burner with automatic throttling and flaring, to a gas holder for intermediate storage, or into a fuel header system.

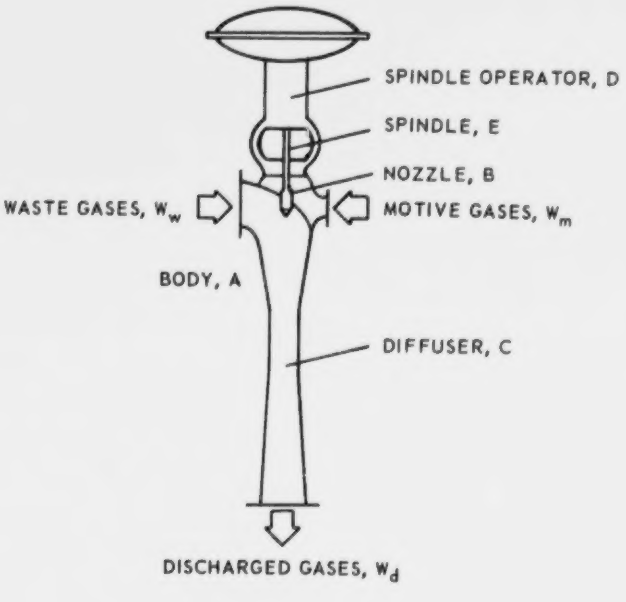


Figure 4-9. Automatic jet compressor.

4.3.3.2 Halogenation

Organic emissions containing a halogen (primarily chlorine) are a special problem, because the halogen atoms are not combustible. Accordingly, incineration of chlorine-containing organic compounds can produce HCl, elemental chlorine, or other chlorinated compounds.

The problem is to design an incineration system that will first produce the hydrogen halide gas and then absorb it. Experimentation has shown that if the hydrogen-to-halogen ratio is high enough, approximately 5 to 1, essentially all of the halogen in the products of combustion will be in the form of the hydrogen halide.

To maintain this ratio for substances like ethylene or propylene dichloride, some hydrocarbon fuel must be added to the combustion system to supply hydrogen. A technique developed to do this for organic chlorides recovers up to 99 percent of the hydrogen chloride as 18° Baumé acid from gas streams containing as little as 3 percent hydrogen chloride.[17]

In this recovery system, the waste is incinerated in a vortex-type burner and immediately quenched in a graphite- or carbon-lined tower; the resulting vapors are processed through a series of impervious, graphite, tubular cascade absorbers, which are designed to produce 18° Baumé acid, with up to 100 ppm of hydrogen chloride in the vent gas. If additional treatment is required, another scrubbing station is provided to produce very weak hydrochloric acid to be used as make-up liquor in the main absorption equipment. The remaining vapors usually contain fewer than 50 ppm hydrogen chloride. This recovery system, depending on the disposal rate, can produce a positive return on investment.

4.3.3.3 Disposal of Waste Gases

Catalytic vapor incinerators at an ethylene producing plant eliminate essentially all ethylene contained in a relatively cool waste gas stream. The heart of the system is a catalyst that makes it possible to burn ethylene that is present in concentrations too low to support normal incineration. The treated stream does not contain catalyst poisons.

Part of the equipment operating costs are recouped by recovering energy released when the ethylene is burned. This energy is recovered in two stages: first, the hot gas stream powers expansion turbines, which drive compressors; then, the stream is reduced to an acceptable heat level for use in power recovery turbines, while the heat recovered is used to super-heat the process steam.

Some plants have adopted other types of incinerators to abate gases and vapors. A direct-flame incinerator is shown in Figure 4–10. The two units burn the organic gases, vapors, and particulate matter in the effluent gases from a phthalic anhydride manufacturing plant.

4.4 PAINT, LACQUER, AND VARNISH MANUFACTURE

4.4.1 Introduction

Paints, lacquers, and varnishes have been used for years for decorative and protective purposes and, in some instances, for electrical insulation and chemical resistance. Present-day coatings are the products of precisely controlled chemical reactions and accurately proportioned formulations, which may include natural or synthetic drying oils, pigments, volatile solvents, resins, driers, thinners, plasticizers, and antioxidants.[18]

Coatings may be divided into two general types: pigmented or nonpigmented. The vehicle (or binder) is common to both types. Most of the materials other than pigments are of organic composition, with varying degrees of volatility. Thus handling, mixing, and processing operations produce different amounts of atmospheric pollution depending on which raw materials are used, the combinations of these materials, and the conditions to which they are subjected.[18]

The paint or varnish manufacturer usually produces his own vehicles by either chemical reactions and/or cooking operations which vaporize part of the ingredients. Other losses result from (1) thinning operations that use volatile solvents and thinners to produce proper consistency for the finished product and (2) the handling and storage of raw materials and intermediate products.[18]

Even with the atmospheric losses involved in manufacture of paints and varnishes, more hydrocarbons usually are emitted from the application of these coatings than from the manufacturing process itself. This source of pollution is covered in Section 4.6.

Production of varnish appears to be the largest contributor of atmospheric hydrocarbon emissions in this industry and thus will be discussed in considerably more detail than paint and lacquer production.

4.4.2 Paint Manufacturing

Paint can be defined as a pigmented liquid composition that is converted to a relatively opaque solid film after application as a thin layer.[19] Enamels are paints which form an especially smooth and glossy film.

Paint manufacturing consists of the following operations:

1. Mixing pigment with sufficient vehicle to make a paste of proper grinding consistency.
2. Grinding the paste on a mill until aggregates are broken down.
3. Letting down (diluting) the ground paste with the remaining materials.
4. Tinting to required color.
5. Testing.
6. Straining, filling, and packaging.

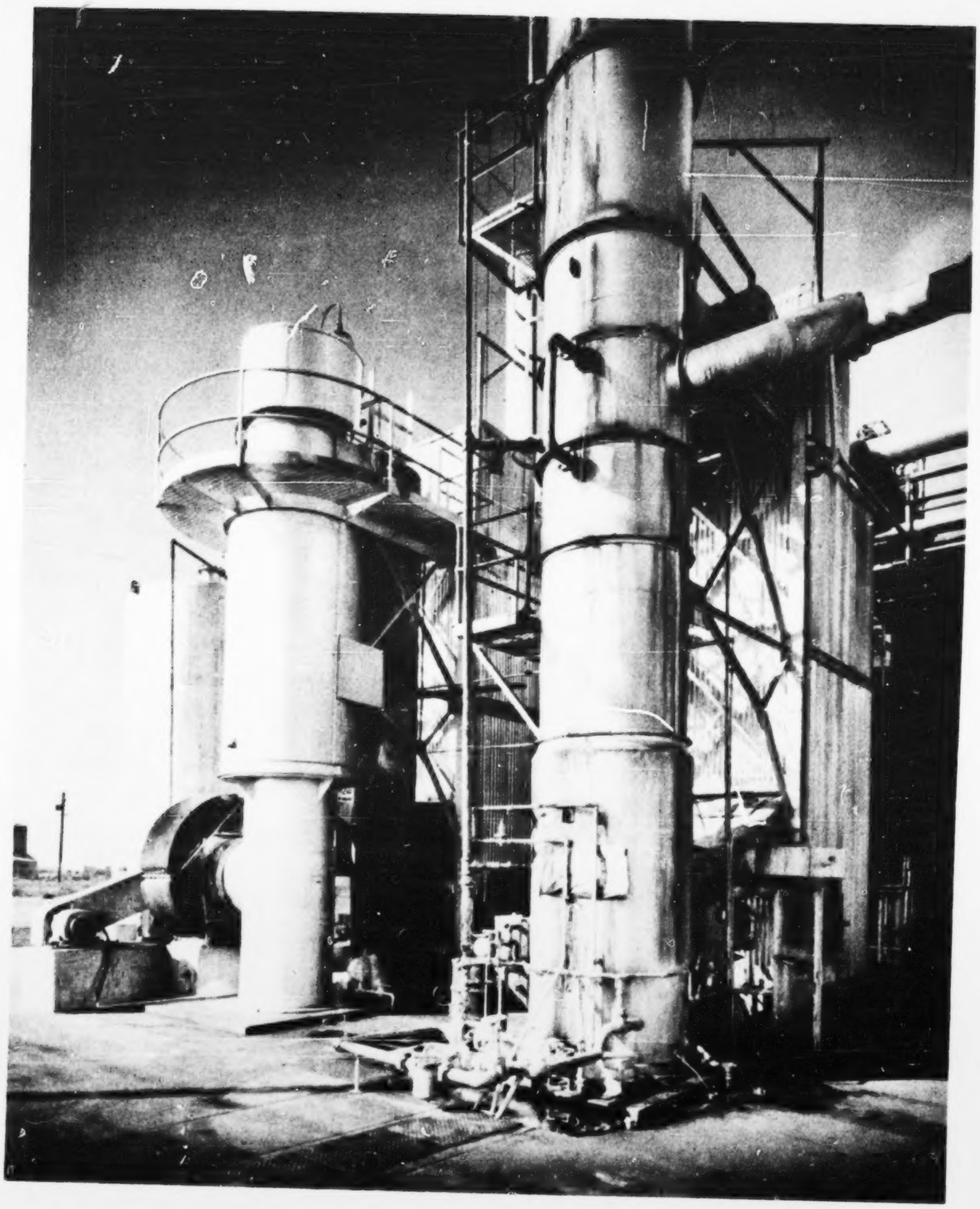


Figure 4-10. Direct-fired afterburner for control of emissions from two phthalic anhydride production units. (Courtesy Reichhold Chemicals, Inc., Azusa, Cal.)

In some cases the mixing and grinding operations are done in one step. Although "grinding" is the term commonly used in the industry, actual grinding or reduction in size of particles of pigment does not occur in the majority of cases.[19]

Paint manufacturing is still largely a batch process because of the large number of raw materials and finished products required, many of which must be custom formulated and processed.[20]

The two sources of hydrocarbon emissions in paint manufacturing are the grinding operation, during which the batch may heat up considerably and lead to vaporization of certain ingredients, and the thinning operation, during which vaporization of solvents occurs. A small amount of pigment fines is emitted from the mixing operation. Thinning of premixed paint pastes to the required consistency for application involves dilution with aliphatic or aromatic hydrocarbons, alcohols, ketones, esters, and other highly volatile materials.[18] Because of the volatility of most thinners, mixing must be done in totally enclosed tanks to prevent losses of these expensive solvents and, more recently, to prevent air pollution from these materials. A recent estimate of the hydrocarbon emissions from paint manufacture is that about 0.5 percent of the weight of the paint is emitted as hydrocarbons. Another estimate is that the solvent loss to the atmosphere from mixing operations generally amounts to no more than 1 to 2 percent of the solvent used.[18]

Methods of controlling atmospheric emissions from paint manufacture include: (1) reformulation of the paint to replace a photochemically reactive solvent such as xylene with a less photochemically reactive solvent, (2) production of water-base coatings, (3) condensation and absorption by scrubbing with water, (4) condensation and absorption by scrubbing with alkali or acid washes, (5) scrubbing and adsorption by activated charcoal or other adsorbents, (6) combustion, and (7) dispersal from high stacks. McFadden states that no one control method is satisfactory for all applications.[21]

The preferred method of controlling the hydrocarbon emissions would be reformulation since this would serve to reduce the reactive solvent emissions during the manufacturing process and during application. Baking enamels cannot, however, meet the requirements of Los Angeles County's Rule 66 by reformulation since baking-oven emissions must be controlled regardless of the solvent used.

4.4.3 Lacquer Manufacturing

Lacquers are solutions of resins in organic solvents that harden as a result of evaporation of the solvent rather than oxidation or polymerization.[20] Present-day lacquers are primarily nitrocellulose coatings, which may be either clear or pigmented. If pigment is added, the lacquer is then called lacquer enamel or pigmented lacquer and is more resistant to weather.

Nitrocellulose is made from cotton linters, which are short fibers remaining on cotton seeds after the long fibers have been removed by cotton gins for textile purposes.[22] Filters are purified by boiling in caustic solution until they become pure white. These fibers are nitrated to produce nitrocellulose, which is the basic film-forming ingredient in lacquers. It is blended with resins, plasticizers, volatile solvents, and diluents to produce lacquers with various properties such as desirable elasticity, good adhesion to surfaces, depth or body of the film, luster, and good drying characteristics. For pigmented lacquers, a separate pigment grinding or milling step is required. Mixing and tinting operations are usually carried out in totally enclosed agitator tanks to decrease the amount of solvent vaporization.

Solvents are the materials that provide the proper consistency for application of lacquers. The solid ingredients of the lacquer as well as the method of application dictate the selection of solvents. The solvents used in lacquer manufacture are mainly the esters, ketones, etc.; the latent solvents used are the alcohols, ethyl, butyl, and amyl; the diluents are the petroleum thinners and coal tar solvents.[22] Usually, blends of several solvents are required to produce satisfactory lacquers.

Resins used in lacquers must be soluble in mixtures of esters, alcohols, and hydrocarbons. Some of the resins used are shellac, elimi, dammar, ester gum, and alkyds.[22]

Hydrocarbon emissions from lacquer manufacture consist of vaporized solvents and diluents; but unless temperatures become elevated, the losses are small. The best method of controlling these emissions is reformulation to replace reactive solvents with less reactive ones. Other methods include condensers, afterburners, scrubbers, absorbers, and adsorbers, or combinations of several of them. For instance, if an activated-carbon adsorber is used, a scrubber should be installed in front of it to remove pitch or a tarry material, which may collect on the carbon and decrease its efficiency.

4.4.4 Varnish Manufacturing

4.4.4.1 Introduction

Varnish has been defined in various ways by the technical societies and several authors.[9,19,22] Some authorities say varnish is a colloid; others say it is a solution. The one common definition, however, is that varnish is unpigmented, consists of resins, oils, thinners, and driers, and dries by evaporation of the solvents and by oxidation and polymerization of the remaining constituents.

The most common varnishes are the oleoresinous ones, which can be broken down into minor classes such as oil plus resins, oil, and oil-modified. They are all solutions of one or more (natural or synthetic) resins in a drying oil and a volatile solvent. All oleoresinous varnishes dry by oxidation; or oxidation and condensation; or oxidation, condensation, and polymerization.[22] The other major type of varnish is spirit varnish, which consists of alcohol solvents plus either natural or synthetic resins with little or no oil. Shellac is the most common example of this type of varnish. Spirit varnishes dry either by evaporation or by evaporation and some polymerization.

Other important types of varnish developed more recently include: alkyd resin varnish, which is a solution of alkyd resin (a synthetic polyester co-reacted with a vegetable oil) in a volatile solvent with added drier; asphalt varnish, which is a solution of asphalt in a volatile solvent; and lithograph varnish, which is used as a vehicle in pigmented lithographing printing ink.

4.4.4.2 Manufacturing Processes and Emissions

The various steps in varnish manufacturing include cooking, thinning, mixing, filtering, storing and aging (if necessary), testing, and packaging. The most important step in this process is cooking. The cooking process performs many functions; some of the most important ones are:

1. Depolymerization of resins and oils. Natural resins are insoluble in many oils, such as linseed, tung, and castor, that are the film-forming materials in oleoresinous varnishes. Thus, the resin must be heated to a temperature above its softening point for decomposition and depolymerization to take place. The resulting resin is then soluble or reacts with the oils.
2. Bodying of natural and synthetic oils.
3. Melting materials to accelerate solubility and reaction.
4. Esterification of rosin, phthalic anhydride, maleic anhydride, or tall oil with a polyhydric alcohol such as glycerol or pentaerythritol.
5. Isomerization to eliminate extreme reactivity in some oils during oxidation.
6. Preparation of alkyd resins.
7. Distillation and evaporation to remove undesirable constituents such as volatiles in resins.

All or part of the above operations take place during the cooking process but differ depending upon the particular batch being processed.

Cooking temperatures in varnish kettles range from 200° to 600°F and are usually maintained for several hours. The average batch starts to give off vapors at about 350° F; the rate of vaporization rises with a temperature increase and reaches its maximum at approximately, or shortly after, the maximum processing temperature is reached.[18,22] Vapor emission continues as long as heating is continued but slowly decreases after the maximum is reached.

There are two types of kettles used for cooking varnish, the open kettle, which is heated over an open flame, and the newer totally enclosed kettle, which is set over or within a totally enclosed source of heat. Naturally, the open kettle allows vaporized material to be emitted to the atmosphere unless hooding and ventilation systems are provided.

The vapors emitted from varnish cookers possess penetrating and disagreeable odors and other irritating characteristics. These vapors consist of (1) low-melting-temperature constituents of natural gums, synthetic acids, and rosins, some of which are purposely driven off for process reasons; (2) thermal decomposition and oxidation products volatilized during bodying of oils; and (3) volatile thinners, which distill off during thinning of hot varnish.[22] The composition of these vapors is a function of the raw materials, cooking formulas, and heating cycle. Some of the raw materials used include (1) oils such as linseed, castor, fish, tall, soya, tung, oiticica, and perilla; (2) resins such as phenolics, rosin, copal, dammar, manila and East India, alkyd, ester gum, acrylates, silicones, epoxies, and polyurethanes; (3) solvents and thinners such as turpentine, xylol, toluol, alcohols, aromatic and aliphatic naphthas, and dipentine; and (4) dryers such as Co, Mn, Pb, and Zn naphthenates; resinates; tallates; and linoleates.

The major constituents of the emissions from varnish cookers are stated to be largely fatty acids and aldehydes, mixed with water vapor, acrolein, glycerol, acetic acid, formic acid, and complex residues of thermal decomposition.[22] The most unpleasant of these is acrolein because of its pungent, disagreeable odor, very low odor threshold, and eye-irritating characteristics. In addition to the air contaminants listed above, some highly offensive sulfur compounds such as hydrogen sulfide, butyl mercaptan, thiophene, and allyl sulfide are emitted when tall oil is esterified with glycerine and pentaerythritol.[7]

Total emissions to the atmosphere depend on the composition of the batch, rate of temperature application, maximum temperature of the process, method of adding solvents and driers, amount of stirring employed, extent of air-blowing, length of cooking time, and amount of pollution or other process control equipment employed. Typical losses from various cooking processes[18] are as follows:

1. Total loss from oleoresinous varnish cooks average 3 to 6 percent, with some losses as high as 10 to 12 percent.
2. Losses from alkyd resin cooks range from 4 to 6 percent.
3. Cooking and blowing of oils produce losses of 1 to 3 percent.
4. Heat polymerization of acrylic resins produces losses of less than 1 percent unless the reaction gets out of control.

For the process of gum-running of natural copals, the amount of vapor liberated is stated to vary from 12 to 35 percent of the original weight of copal, depending upon the type of copal, temperature, and duration of the running process.[23] A reasonable average is stated to be a 25 percent loss.

The second largest source of emissions from varnish manufacture is the thinning operation. Many processes require the addition of solvents and thinners during the cooking process which is near the boiling point of the solvents. The amount of solvent lost to the atmosphere in this case will be considerable if the open kettle operations are used. However, other factors controlling the solvent loss include its volatility, the temperature of the material to which it is added, the amount of additional heat applied, if any, and the degree of stirring employed. Because of the volatility of most solvents, most thinning operations must be done in totally enclosed tanks to prevent large losses of the solvents. This is necessary because most of these solvents are not only pollution problems, but are quite expensive. The method of thinning also affects the total solvent loss because if a small amount of cold solvent is poured into a large mass of hot varnish, more solvent is vaporized and lost than if a small amount of hot varnish is poured into a large volume of cold solvent.

Losses of solvents during thinning can range from 5 to 50 percent of the total added in open thinning tanks, depending upon the method used and the amount of time the thinned mixture is left open.[23] However, since most manufacturers use totally enclosed thinning tanks, the amount of solvent lost to the atmosphere amounts to no more than 1 to 2 percent of the solvent used.[18]

4.4.4.3 Controls

It is apparent from the foregoing survey of varnish-making and synthetic resin-making processes that there are many opportunities for release of gaseous materials, which for various reasons it is desirable to control. Generally, the varnish industry has practiced control of emissions because of economic reasons. In fact, integral condensers reduce emissions from many processes considerably. Other methods of controlling these emissions include scrubbers, absorbers, adsorbers, afterburners, reformulation of solvents, and sublimation.

In designing condensers to control emissions from varnish-making operations, the standard design factors such as the type(s) of compounds and their physical properties, such as temperature, volume, concentration, vapor pressure, and specific heat must be considered. In addition, in many of these processes noncondensible substances must be removed by other means. Many of the lower-boiling-point noncondensible hydrocarbons are very inflammable, and provision must be made to remove the risk of flashes. For example, to remove copal vapors, a satisfactory condensation unit should include the following:[23]

1. A condenser to remove most of the vapors, followed by scrubbing and combustion, charcoal adsorption, or a ventilating stack to remove the traces.
2. Means for vapor withdrawal.
3. Provision for cooling and collecting a large volume of distillate.
4. Corrosion-resistant materials of construction.
5. Precaution against flashes.
6. Provision for overflow between cooking kettle and first condenser.
7. Recirculation of cooling water to reduce quantities required.
8. Separate unit for each kettle if possible.

Both surface-type and direct-contact-type condensers have been employed in this industry.

Several different types of scrubbers have been used by the varnish industry.[23] These include (1) a countercurrent device in which the vapors enter at the bottom against a descending water stream and leave through the top, (2) a parallel-current water scrubber succeeded by smaller counter-current scrubbers, (3) water jet scrubbers, and a (4) scrubber with spinning discs located on a revolving vertical spindle.

Adsorbers used in this industry are very efficient at removing solvents and odors from varnish-making processes; however, to maintain high efficiencies, the gas streams entering these units must be essentially free of solids and entrained oil droplets. In varnish-making, the effluent is not free of these materials, and in practice a pitchy deposit forms on the charcoal absorbent. This deposit resists removal by steam during desorption.[23] In another case this pitchy material was also found and assumed to consist of tarry materials that found their way past the preliminary scrubber plus low-molecular-weight materials undergoing polymerization.

In controlling varnish vapors, it appears that adsorption by charcoal or other solid adsorbents would be most useful after the bulk of condensible matter has been removed by condensers, scrubbers, etc. Sevard states that adsorption, following revivification, provides concentrated vapors, which may be burned more economically than when mixed with large volumes of air.[24]

At present, the most effective means of controlling emissions from varnish-making operations has been combustion. Vapor disposal by combustion has several advantages over other control methods because it requires a minimum of equipment, assures complete vapor elimination from the atmosphere, and consumes very little fuel in correctly designed furnaces. Incineration, of these hot combustible vapors calls, however, for special devices to protect against flame propagation in the opposite direction of the flow of vapors between the kettle and the incinerating furnace. In some systems, a series of water jets or a water scrubber are interposed between the varnish kettle and the furnace.[23] In another system, the vapors are passed first through a water-cooled condenser and then to a combustion hearth.[23] In still another, the varnish vapors are assisted from the kettle by means of a steam nozzle. The mixture of steam and vapor is condensed. The reduced pressure, which results from the vapor condensation pulls the vapors from the kettle. The noncondensibles are then burned.[23]

In designing afterburners to control emissions in a process where the ratio of noncombustibles to combustibles is relatively large, five interrelated variables[25] must be considered: reaction temperature, particle size of combustibles, mixing, flame contact, and residence time. The importance of these variables is apparent since theories of flame propagation propose that a flame is maintained by continuous autoignition at the flame front.[25]

In designing an afterburner control system for varnish kettles, the following items should be considered:

1. Hooding. Hoods should be tight fitting, should be easy to clean, and should prevent condensate drippage into the kettle.
2. Ductwork. Ducts should be sloped away from the hoods, and low spots should be eliminated. Corrosion-resistant materials with provisions for cleaning should be used.
3. Flashback Protection and Precleaning. A water spray leg is recommended for precleaning and flashback protection. A high-velocity section at inlet provides additional fire protection.
4. Afterburner. A minimum gas temperature of 1200°F should be used with provisions for temperatures of 1400°F. Intimate mixing with luminous flame should be provided. Combustion chamber should be refractory lined and should provide residence time of 0.5 second. The velocity through the chamber should not be less than 15 feet per second.
5. Controls. Burner controls should be of modulating type to insure a continuous and uninterrupted flame.
6. Safety. Protection must be provided for all possible types of failure of the control system to prevent fires.

An example of a typical control system used in a Los Angeles varnish manufacturing plant is shown in Figure 4-11.

Two afterburner installations at varnish manufacturing plants have been tested.[25] A tangentially fired system was found to provide over 99 percent efficiency with regard to gaseous organic matter calculated as hexane. This unit cost $6,500 when it was installed in 1956. Fuel requirements are 1,980,000 Btu per hour, which amounts to a cost of $0.90 per hour to incinerate 950 standard cubic feet per minute of contaminated air. An axially fired afterburner had an efficiency of 96 percent when removing gaseous hydrocarbons as indicated by the modified Beckman Model 2 infrared spectrophotometer. This afterburner cost $2,500 installed. Fuel requirements are 570,000 Btu per hour, which amounts to a cost of $0.26 per hour.

Catalytic combustion units have also been considered in the varnish industry. However, one test showed that a temperature of 950°F was required to remove all odors.[7] Since this temperature is near the 1200°F required in the direct-flame type, the advantage in fuel saving of using this type unit is questionable.

Solvents emitted from thinning operations can be controlled by the methods discussed under paint manufacture. Again, the best method is to reformulate the mixture to

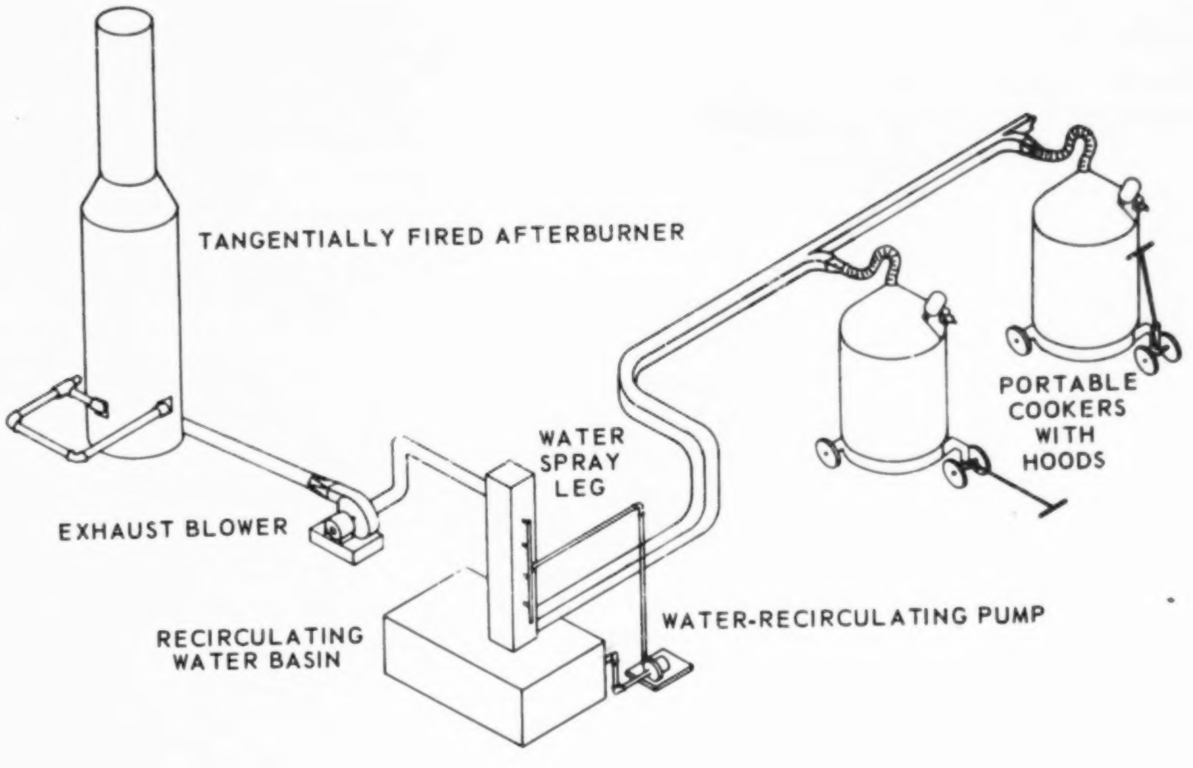

TANGENTIALLY FIRED AFTERBURNER
PORTABLE COOKERS WITH HOODS
WATER SPRAY LEG
EXHAUST BLOWER
WATER-RECIRCULATING PUMP
RECIRCULATING WATER BASIN

Figure 4-11. Schematic plan for varnish-cooking control system.

substitute a less reactive solvent for a reactive one.

4.5 RUBBER AND PLASTIC PRODUCTS MANUFACTURE

4.5.1 Introduction

The rubber and plastic industries are similar in that many ingredients other than the base material are added to produce desired properties of the final product. The ingredients are classified according to the part they play in the finished product. Some of the ingredients, however, may have several functions, so this classification is arbitrary. The compounding ingredients added to rubber are as follows: (1) plasticizers or softeners, (2) vulcanizing agents, (3) accelerators, (4) activators and retarders, (5) antioxidants, (6) fillers, and (7) miscellaneous ingredients such as pigments, rubber substitutes, odorants, abrasives, stiffeners, and blowing agents.

Vinyl chloride polymers and copolymers are thermoplastics that are naturally hard, but can be changed to permanently pliable materials by addition of suitable plasticizers. The most common plasticizer used for this purpose is dioctyl phthalate (DOP), but sometimes diisoactyl phthalate (DIOP) is used. For flexible plastics and sponges, there are 50 or more parts of placticizers per 100 parts of resin. These products are cured at high temperatures, which volatilize the placticizers and produce air pollutants.

4.5.2 Rubber Manufacture

The most important operations in the manufacture of rubber are as follows: (1) physical treatment of raw rubber to prepare it for addition of compounding ingredients; (2) incorporation of various substances, especially fillers; (3) pretreatment of mix to make it satisfactory for preparing the final product; (4) forming the final product; and (5) vulcanization or curing the molded article.

The first step in this process is plasticization which can be done in several ways. Mechanical plasticization is accomplished on a mixing mill or internal mixer which rolls the rubber and makes it soft and plastic. Heat plasticization is accomplished by heating in ovens for about 24 hours at 300° to 400°F. Chemical plasticization is accomplished by adding peptizing agents on the mills and is more rapid and economical than other means under certain conditions. Typical peptizing agents are naphthyl mercaptan, xylyl mercaptan, zinc salt of pentachlorothiophenol, and dithio-bis-benzanilide.

Typical antioxidants that create hydrocarbon and organic pollutants are aromatic amines, aldehyde-amine condensation products, derivatives of secondary naphthylamines, aromatic diamine derivatives, and ketone-amine condensation products.

To vulcanize or cure the molded article, the material is held at elevated temperatures of 200° to 300° F from a few seconds to several hours. This is the operation during which many of the plasticizers, accelerators, and other organics are volatilized and driven off as air pollutants. One of the major problems associated with rubber production is odor.

The principal methods used to control air pollutants from rubber manufacture are those discussed in Section 4.4 for solvent recovery: reformulation, condensation, adsorption, absorption, and incineration. Many of the rubber manufacturers have been recovering solvents for economic reasons. In one case, a rubber company installed an activated-carbon adsorption system and found that with a 65 percent recovery figure for a base, the system could save them up to $39,000 in the first full 12 months of operation.[26]

In reformulation, use of nonreactive solvents in place of reactive ones would alleviate hydrocarbons and odor problems.

Direct-flame incineration has proved to be very successful in controlling both hydrocarbons and odors. In one rubber processing plant, tests of a direct-flame incineration system showed that for a total system flow of 31,000 pounds per hour, and an incineration temperature of 1,120° F, total hydrocarbons were reduced from 1,305 to 207 ppm by weight with an efficiency of 84 percent[27] (calculations based on reduction of total hydrocarbons in pounds per hour). With allowance for the contribution of fuel oil, as established during the blank run, the efficiency of process contamination removal became 89 percent. This was stated to be closer to the overall efficiency expected if the incinerator were fired with natural gas.

In a similar run at an incineration temperature of 1,190° F, total hydrocarbons were reduced from 1,155 to 89 ppm by weight for an efficiency of 92 percent. Allowing for fuel oil contribution would increase this efficiency to 97 percent.

Catalytic-type combustion has been investigated thoroughly for removing pollutants from rubber plants. In some cases, however, it has been found that temperatures only 100°F below those required for direct-flame incineration were required, and thus increased costs of catalyst-type operations would not be justified. In other tests,[27] this type of combustion was abandoned because of (1) the danger of poisoning of the catalyst and (2) the impairment of its effectiveness as the catalyst became coated with carbonaceous deposits.

4.6 SURFACE COATING APPLICATIONS

4.6.1 Introduction

Coatings applied to surfaces for protection and decoration can be broadly divided into two classes: convertible and nonconvertible.[28] The convertible class includes oil paints and oil varnishes in which the coating dries and hardens primarily through oxidation and polymerization reactions induced by the surrounding air. The nonconvertible coatings are those in which a resinous film-forming material is dissolved in a volatile solvent. When applied to a surface, the solvent evaporates and leaves a resin film, which does not undergo any significant chemical change on continued exposure.

Solvents facilitate the use of the varnishes and resins that form both classes of coatings noted above. In coatings use, the quantity of solvent purchased generally coincides with the quantity emitted into the atmosphere. Materials referred to in the trade as diluents and thinners are also included in the general category of solvents for coatings applications. Most of the organic solvents in commercial or industrial use can be classified as aliphatic hydrocarbons, aromatic hydrocarbons, alcohols, ketones, esters, halogenated hydrocarbons, or mixtures of these categories of compounds.

4.6.2 Emissions

When coatings are applied, no attempt is usually made to collect emissions, and essentially all of the solvents used find their way into the atmosphere.

Certain coating operations are amenable to control. These include industrial finishes requiring baking, coating coils, enameling wire, painting automobiles, painting other sheet metal products, and drying in lithograph ovens.

4.6.3 Control Techniques and Costs

The use of nonreactive formulation (e.g., water-base and formulations with nonreactive organic solvents) is the best approach to control of these emissions in general. Organic emissions from the multitude of painting and baking operations employed in metal finishing can be reduced or suitably controlled by a variety of methods. The methods that warrant consideration are modification of equipment, reformulation of solvents, adsorption, absorption, and incineration.

The possibility of reducing or eliminating air pollution through equipment or process modification should be thoroughly evaluated. This method offers an opportunity for significant cost savings either by eliminating the need for special control equipment or by reducing the size of the control equipment ultimately required.

When the possibilities for modification of equipment and process have been exhausted, the recovery or control of the remaining solvent emissions can theoretically be accomplished by one or more of the following processes: condensation by cooling or compression, absorption, chemical modification including incineration, and adsorption.

All these systems were studied in detail in order to select and investigate experimentally the method that appeared to have the greatest promise of feasibility for control of solvent emissions where the concentrations range from 100 to 200 parts per million.[29]

It has been shown that for condensation of organic vapors by cooling, refrigeration requirements would be very costly. For example, to obtain 90 percent recovery of toluene vapors being emitted at a rate of 250 pounds per day with a concentration of 1 pound per 40,000 cubic feet of air would require over 500 tons of refrigeration.

The use of compression to accomplish condensation would require high pressure and large power consumption. In the toluene example above, over 800 atmospheres pressure and 70 horsepower per thousand cubic feet per minute handled would be required.

Absorption involves the scrubbing of the vapor-laden gases with a liquid in which the solvent is soluble. With organic vapors, mineral oil would be a possible absorbing agent. In this case, also, impractically large absorption equipment would be required for organic vapors in the 100- to 200-ppm range.

Chemical destruction or modification of organic vapors would require impractically large equipment because of difficulties similar to those involved in absorption. Destruction of organic vapors by incineration becomes very costly for the range of concentration of organic vapors occurring in surface coating operations. With higher concentrations, such as are emitted from paint baking ovens, incineration has been used with success because of lower fuel requirements and some heat recovery.

The control of organic solvent emissions from protective coating operations was investigated in a pilot plant study by Elliot[30] et al. It was concluded that the control of organic emissions from spraying operations was technically feasible using adsorption on activated carbon. By using the data obtained in the pilot plant adsorber, estimates were made of costs for larger units. These estimates ranged from $8.00 per cfm for a 1,000-cfm spray booth to $1.54 per cfm for a 50,000-cfm spray booth.

For baking ovens and other operations that can use afterburners, several factors are important in the selection of a proper system. Because an afterburner, or almost any other air pollution equipment, does not yield a profit, the tendency in some cases is to buy the cheapest equipment on the market. The cheapest equipment may not always be the most economical to operate over an extended period.

One way to reduce the cost of an afterburner is to reduce the amount of exhaust air to be treated. Fire underwriters' standards require that vapor concentrations inside the oven be kept at not more than 25 percent of the lower explosive limit of the vapor. When an afterburner is to be added to an existing oven, a check should be made to determine whether the amount of dilution air actually being used is substantially more than that required by the underwriters' standards, as is sometimes the case. The afterburner can then be designed or selected for the required volume. When a new oven is to be designed for afterburner control, the oven and afterburner can be designed as an integral unit, with the afterburner furnishing all or part of the heat required to operate the oven.

Afterburners generate a lot of waste heat, and the need for heat recovery systems is apparent. For afterburners handling large air volumes (3,000 cfm or more), the addition of heat recovery systems is almost a necessity. In principle, there are three types of heat recovery systems: self-recuperating heat recovery, heat recovery to provide hot process air for the ovens, and heat recovery to provide heat for auxiliary use. The most common system is the self-recuperating heat exchanger, which can be built into the incinerator as a neat package. Three types are in use, as shown in Figures 4-12, 4-13, and 4-14. In Figure 4-12, all the exhaust air passes through the heat exchanger. With this arrangement, only one heat exchanger efficiency can be obtained. The system shown in Figure 4-13 allows part of the incinerated air to be bypassed. Heat exchange efficiency is controlled by controlling the bypass volume. The system in Figure 4-14 employs a variable-type heat exchanger (for example, Ljungstrom), which allows the efficiency of heat exchange to be varied. Self-recuperating heat exchangers should be sized to take over most of the heat load, but they should not be too large. Even at maximum loading, the incineration temperature should be controlled by the burner and not by the concentration of solvents.

An incinerator system can be designed in many ways. For this reason, some basis for comparison of designs is necessary. While direct comparison is not possible, a few rules should be applied to their comparison.

4.7 DEGREASING OPERATIONS

4.7.1 Introduction

In many industrial operations, metal parts must be thoroughly cleaned of all grease and oil before they can be plated, painted, or further processed. In this connection, it is important to recognize the terminology used by industry to differentiate between various cleaning processes in which organic solvents are used as cleaning agents. For example, certain types of process equipment operate with little or no built-in control of solvent losses, while others operate with a relatively high degree of control with regard to solvent losses. In general, "degreasing" merely implies the use of an organic solvent to dissolve and remove soils from metals, etc., by any type of process. If the solvent used for cleaning is at or near room temperature and if the equipment used is not designed to control solvent losses, then such a process is referred to as "solvent cleaning" or "cold solvent cleaning." The solvents used in these processes may be halogenated, nonhalogenated, or mixtures of them. If the solvent used for cleaning is maintained by heat input at its atmospheric boiling point in the process equipment, and if this equipment is designed to control and minimize solvent losses to the air, then the cleaning process is called "vapor degreasing". In other words, vapor degreasing is a specific

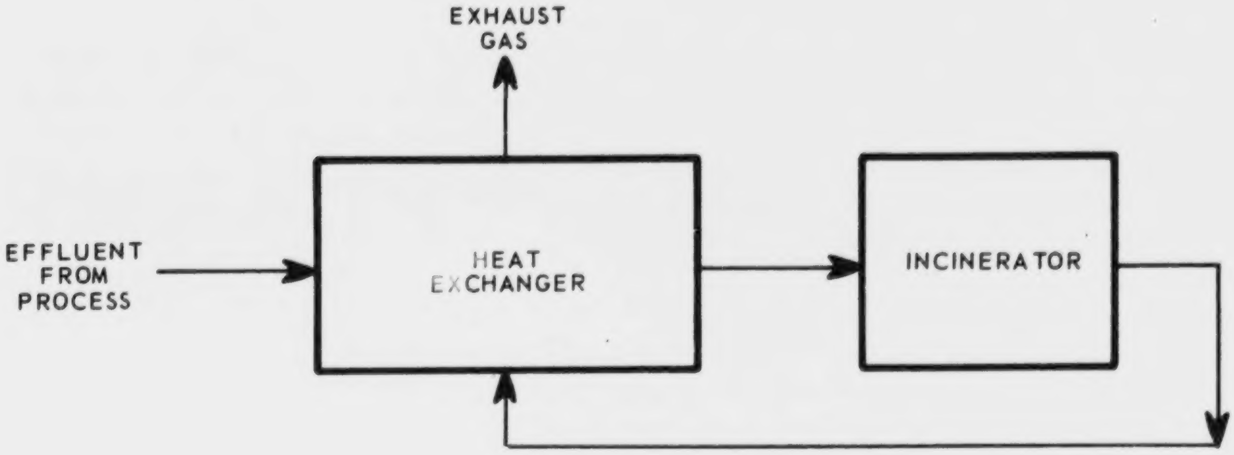
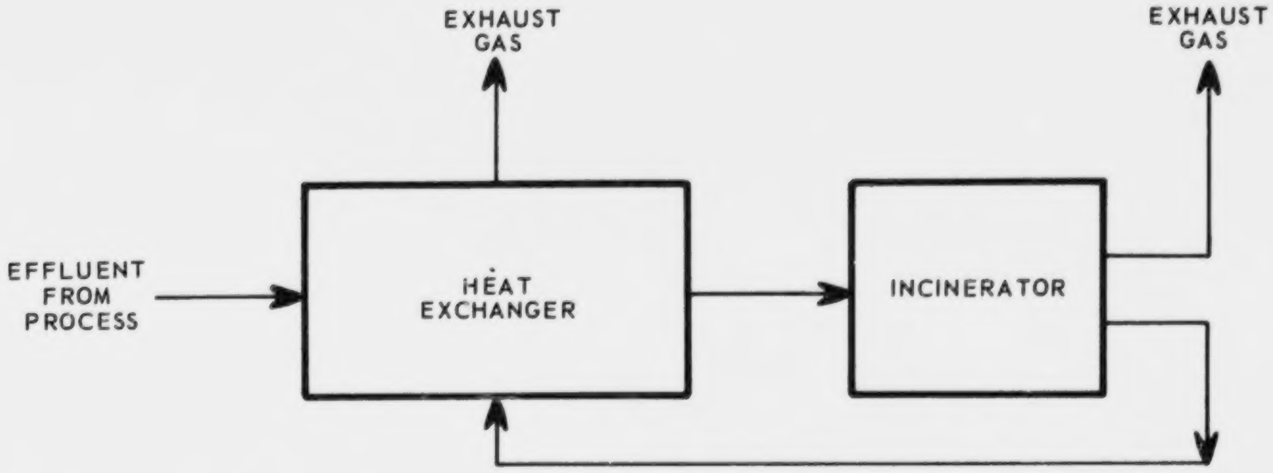

EXHAUST
GAS
EFFLUENT
FROM
PROCESS
HEAT
EXCHANGER
INCINERATOR

Figure 4-12. Self-recuperating heat recovery: single efficiency heat exchange.


EXHAUST
GAS
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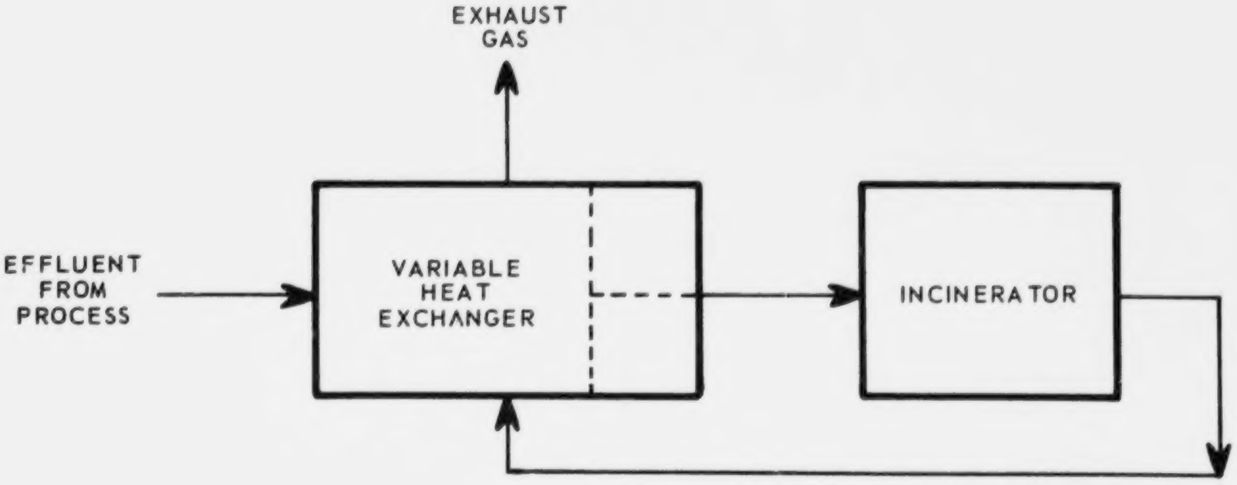
EXCHANGER
INCINERATOR

Figure 4-13. Self-recuperating heat recovery: variable heat exchange.


EXHAUST
GAS
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FROM
PROCESS
VARIABLE
HEAT
EXCHANGER
INCINERATOR

Figure 4-14. Self-recuperating heat recovery: variable efficiency heat exchange.

type of cleaning process designed to use only halogenated solvents, which are essentially nonflammable and have a relatively high vapor density. Complete descriptions of "solvent cleaning" and "vapor degreasing" are presented in the chapter on metal cleaning in the *Metals Handbook.*[31]

With respect to "vapor degreasing" operations using trichloroethylene, for example, industrial experience indicates the following general guidelines can be used in estimating solvent vapor losses from a properly designed and operated machine:

1. Based on the open cross-section area of the degreaser, estimate the operating solvent loss as 0.25 (± 50 percent) pound per hour per square foot of open area.
2. Based on the work load processed through the unit, estimate solvent loss as 0.5 to 1.5 gallons per hour per ton of metal cleaned.
3. Based on the solvent turnover in the unit (boil-up rate), estimate solvent loss as 1 to 2 percent of the vapor generation rate in pounds per hour.

Emissions from all types of degreasing operations consist of vapors of the solvent or solvents used in the cleaning process. While daily emissions from a single unit vary from a few pounds to as high as 1,300 pounds for a spray degreasing booth, the total emissions from such sources in an industrialized area may be quite large.[7] It has been estimated that in Los Angeles County, degreasing vapors amounted to 95 tons per day in 1967.[32]

4.7.2 Vapor Degreasing Equipment

The usual vapor degreaser includes a heating system on one end of the tank to create a vapor that condenses on the metal parts. Condensation continues until the metal is heated to the vapor temperature. The upper portion of the tank contains water-cooled condensers to prevent excessive loss of vapors. Because of the high density of the vapors, they do not tend to rise from the tank if excessive drafts are prohibited.

Because of the specialized equipment design features required for satisfactory operation and control of vapor degreasers, commercial rather than "handmade" units should be used. In general, suppliers of vapor degreasing equipment can provide so-called "standard" units, or can design specific equipment for almost any process requirement. The vapor degreasing process lends itself equally well to batch and continuous type operation. Also, a variety of different cleaning cycles (using the separate vapor and liquid phases, as well as liquid sprays) may be incorporated in any given vapor degreaser as required by the cleaning process.[33] A thorough discussion of vapor degreaser design, operation, maintenance, and safety are presented in the ASTM *Handbook of Vapor Degreasing.*[34]

A relatively new development in controlling vapor loss from a vapor degreaser is the incorporation of an additional lower temperature cooling surface (chiller) in the freeboard section of the machine. This is claimed to reduce operating solvent loss by as much as 35 to 50 percent.

A review article on the industrial safety experience of trichloroethylene as a vapor degreasing solvent is available.[35]

Degreasing tanks can be equipped with sliding or guillotine-type covers, which can be closed when not in use.

Since most degreasing solvents are slightly toxic, some degreaser tanks are provided with an exhaust system to capture escaped vapors. These lateral exhaust hoods should be designed in accordance with the ventilation rate outlined in the American Standard Safety Code for Ventilation and Operation of Open-Surface Tanks, Standard #Z9.1-1951. The ventilation rates should be for Class B-3 operations, and the ventilation rates should not exceed those specified in Tables 3 and 4 of the standard.

4.7.3 Control Systems and Costs

In general, no auxiliary control systems are used on vapor degreasers, and in Los Angeles County most processors have switched to noncontrolled solvents to comply with the organic emission regulations. Switching, for example, to a less reactive, higher-boiling-point solvent such as perchloroethylene has made it possible for vapor degreasing operations to operate within the law.

To minimize solvent losses from vapor degreasers, the following techniques[34] should be followed:

1. A degreaser should not be subject to drafts from open windows, doors, unit heaters, exhaust fans, and so forth; therefore, if possible, a 12- to 18-inch-high shield should be placed on the windward side of the unit.
2. Work items should be placed in the basket in such a way as to allow efficient drainage and prevent carryout of solvent.
3. Metal construction should be used for all baskets, hangers, separators, and so forth; use of rope and fabric that absorb solvent should be avoided.
4. The speed of work entering and leaving the vapor zone should be held to 11 feet per minute or less; the rapid movement of work through the vapor zone causes vapor to be lifted out of the machine.
5. Spraying above the vapor level should be avoided; the spray nozzle should be positioned in the vapor space where it will not create disturbances in the contents of the vapor.
6. Work should be held in the vapor until it reaches the vapor temperature at which all condensation ceases; removal before condensation has ceased causes the work to come out wet with liquid solvent.
7. When the metal articles are of such construction that liquid collects in pockets, the work should be suspended in the free-board area above the tank to allow further liquid drainage.
8. The degreaser tank should be kept covered whenever possible.

In general, carbon adsorption is not used on exhaust systems from vapor degreasers. Adsorbers are used more extensively on exhaust streams from other types of solvent cleaning processes for both halogenated and, in particular, nonhalogenated organic solvents.[36,37] In one case, a system consisting of two parallel-flow carbon chambers removed 1,100 gallons of solvent per month from the vapor-laden air exhaust from spray degreasing booths.[7] This unit cost about $9,000 and has a flow capacity of 3,000 cubic feet per minute.[38]

4.8 DRY CLEANING

4.8.1 Introduction

Clothing and other textiles may be cleaned by treating them with organic solvents. This treatment process involves agitating the clothing in a solvent bath, rinsing with clean solvent, and drying with warm air.

There are basically two types of dry-cleaning installations: those using petroleum solvents (Stoddard and 140°F), and those using chlorinated synthetic solvents (perchloroethylene). Early dry-cleaning plants used petroleum solvents. Because of the inherent fire hazard, most zoning laws prohibit the operation of cleaning plants that use petroleum solvents in residential and commercial areas. Nonflammable, chlorinated solvents were developed for use in residential installations. Chlorinated solvents do, however, have several disadvantages: higher costs (tenfold more expensive), greater toxicity, more corrosive to metals, and more deleterious to some dyes and fabrics. Nevertheless, the trend is toward synthetic solvent plants both for small and large installations.[7]

Based on an average per capita emission rate of 3.9 pounds per year,[39] total organic emissions from dry cleaning are on the order of 400,000 tons per year in the United States.

4.8.2 Process Description

In a petroleum-solvent dry-cleaning plant, the equipment generally consists of a washer, centrifuge (extractor), tumbler, filter, and often a batch still. The centrifuge is used to recover solvent by spinning it from the clothes. The clothes then enter a tumbler where they are dried with warm air. The tumbler is usually vented through a lint trap to the atmosphere in this type of plant.

In synthetic solvent plants, the washer and extractor are a single unit. The tumbler operates as a closed system, having a condenser for vapor recovery. The tumbler is vented to the atmosphere or to a carbon adsorber only during a short deodorizing period.

4.8.3 Solvent Emissions

The major source of solvent emissions in dry cleaning is the tumbler through which hot air is circulated to dry the clothes. Drying leads to vaporization of the solvent and emissions to the atmosphere, unless control equipment is used. Because of the volatility of the solvents used, additional emissions occur when storage tanks are loaded, equipment doors are opened, ductwork or equipment leaks, and solvent-soaked textiles are removed from equipment. These latter sources are more of a problem in petroleum plants because the low cost of the solvent does not give much economic incentive for conserving the solvent during handling operations.

Since dry cleaning is only a physical process, solvent emissions consist of the respective evaporated solvents. Chemical composition of petroleum solvents is about 46 percent paraffins, 42 percent naphthenes, and 12 percent aromatic compounds. In Los Angeles, Rule 66 led to reformulation of the solvents to reduce the aromatic content to less than 8 percent.

Emissions from synthetic plants using separate vessels for cleaning and drying are about 10 gallons per 1,000 pounds of textiles cleaned. This drops to 2.5 to 3.5 gallons per 1,000 pounds for older plants in good condition but with carbon adsorbers, and down to only 1-1.5 gallons per 1,000 pounds of textiles for new integrated plants with activated-carbon adsorbers.[38] The rate for units using the same vessel for cleaning and drying units is in the range of 5 gallons per 1,000 pounds of textiles cleaned without adsorption units. Emissions from petroleum-solvent plants are about 15 gallons per 1,000 pounds of textiles.[7] The relative emission contribution on a solvent tonnage basis is somewhat smaller, because a gallon of synthetic solvent is about twice as heavy as a gallon of petroleum solvent.

4.8.4 Control Techniques and Costs

Both adsorption and condensation systems may be used to control solvent emissions from dry-cleaning plants using synthetic solvents. Solvent recovery systems are not only commercially available as part of a synthetic solvent cleaning plant, but they are also economically attractive. The primary control element is a water-cooled condenser, which is an integral part of the closed cycle in the tumbler or drying system. Up to 95 percent of the solvent that is evaporated from the clothing is recovered here. About half of the remaining solvent is then recovered in an activated-carbon adsorber, giving an overall control efficiency of 97-98 percent. Because of the value of the recovered solvent, the adsorption unit pays for itself within 1 to 2 years in all except the very smallest units.[7] A double-bed activated-carbon unit handling 700 cubic feet per minute and equipped with low-pressure steam regeneration costs about $2,300.[38] Despite this economic advantage, only about half of all synthetic solvent cleaning units are thought to have carbon adsorbers. In Los Angeles County, it is estimated that 50-75 percent of all units have adsorbers and that these account for 25 percent of total dry-cleaning volume.

There are no commercially available control units for solvent recovery in petroleum-solvent plants because it is less economical to recover the vapors. The vaporized solvent is not condensible at the temperatures employed, and thus the whole solvent recovery burden would fall on an adsorption system, necessitating equipment up to 20 times larger than that used in a comparable synthetic solvent plant. One recent estimate shows the solvent recovery cost to be about 1.7¢ per pound of clothing;[41] however, even with this cost, it would appear that petroleum plants could install solvent collection equipment and remain competitive with synthetic plant operations, since total operating costs account for only about 20 percent of the overall dry-cleaning cost.

Another way of controlling solvent emissions from petroleum plants is through direct-fired afterburners. Estimates show that a saving in capital cost could be achieved, but an increase in operating costs would also be incurred compared to carbon adsorbers.[41] Afterburners are not suitable for synthetic chlorinated hydrocarbons because of the danger of producing hydrogen chloride, phosgene, or other toxic gases.

4.9 STATIONARY FUEL COMBUSTION

4.9.1 Introduction

The combustion of fuels may result in the emission of hydrocarbons and other organic material if combustion is not complete. When properly operated and designed, however, stationary fuel combustion equipment is not a large source of organic emissions, and control equipment is not required.

4.9.2 Processes and Emissions

Fuels are burned in a wide variety of equipment ranging from small hand-fired coal furnaces to large oil, gas, and coal-fired steam-electric generating plants. Due to variations in combustion efficiency and type of fuel, hydrocarbon emissions will depend on the particular type of combustion device. Table 4–4 presents the average hydrocarbon emissions for various types of fuels and furnace sizes. Considerable variation in these emissions can occur, however, depending on the operation of an individual unit.

4.9.3 Control Techniques

Hydrocarbon emissions from fuel combustion can be reduced or eliminated by essentially three techniques: improved operating practices, improved equipment design, and fuel substitution.

4.9.3.1 Operating Practices

Good operating practice is the most practical technique for reducing hydrocarbon emissions from existing stationary combustion sources. Even the best equipment will perform poorly if improperly applied, installed, operated, or maintained and emit hydrocarbons, smoke, and other pollutants. Hydrocarbon emissions are directly related to the three common combustion parameters of time, temperature, and turbulence. A high degree of fuel and air turbulence will greatly reduce hydrocarbon emissions, increase combustion efficiency, and reduce fuel consumption.

Guidelines for good combustion practice are published by the fuel industry, equipment manufacturers, engineering association, and government agencies. Stationary combustion units should be operated within their design limits at all times and according to the recommendations of the manufacturer in order to achieve a high degree of combustion efficiency. Combustion units and components should be kept in good repair to meet design

Table 4–4. AVERAGE HYDROCARBON EMISSIONS FROM STATIONARY FUEL COMBUSTION SOURCES[a] (lb/10^9 Btu)

Fuel	Size range		
	Steam-electric	Industrial	Domestic and commercial
Coal	7.7	38	380
Oil	5.3[b]	12.5	12.5-19
Gas	Neg.	Neg.	Neg.

[a] Expressed as methane; based on data from reference[39], except as noted.

[b] Datum from reference 40.

specifications. Flue gas monitoring systems such as oxygen and smoke recorders are helpful in indicating the operation of the furnace and are useful in keeping emissions at a minimum.

Source of information on good operating practice include:

1. American Boiler Manufacturers Association.
2. American Gas Association.
3. American Petroleum Institute.
4. American Society of Heating, Refrigerating, and Air-Conditioning Engineers.
5. American Society of Mechanical Engineers.
6. The Institute of Boiler and Radiator Manufacturers.
7. Mechanical Contractors Association of America.
8. National Academy of Sciences - National Research Council.
9. National Coal Association.
10. National Fire Protection Association.
11. National Oil Fuel Institute.
12. National Warm Air Heating and Air-Conditioning Association.
13. U. S. Bureau of Mines.

4.9.3.2 Improved Equipment Design

Hydrocarbon emissions may be reduced by upgrading combustion processes through improving designs to reduce emissions or through redesign to reduce the quantity of fuel required for a given energy output.

Improvements in the combustion of pulverized coal and better mixing of highly turbulent secondary air into the primary combustion zone have improved combustion efficiencies and reduced emissions of hydrocarbons from steam-electric generating plants. The trend toward better steam utilization in these plants has also improved the efficiency of conversion of thermal energy from fossil fuels into electrical energy. Table 4–5 shows recent improvements in efficiency of fossil fuel combustion for electric generation.

Table 4–5. TRENDS IN OVERALL EFFICIENCY OF STEAM-ELECTRIC GENERATING PLANTS [42,43] (Btu per kw-hr)

Year	Coal	Oil	Gas
1956	11,257	12,828	12,245
1957	11,191	12,512	12,238
1963	10,258	11,278	11,066
1964	10,241	11,138	10,962
1965	10,218	11,097	10,868
1966	10,301	11,247	10,774

Continued research in the areas of magnetohydrodynamics, electrogas dynamics, and fuel cells, solar energy, etc., offers the promise of reduced fuel requirements and reduced hydrocarbon emissions.

4.9.3.3 Fuel Substitution

The substitution of gas for coal or oil in any type of furnace reduces the emissions of organic gases when good combustion techniques are used. A switch from coal to oil will reduce organic emissions on smaller industrial furnaces and on commercial and domestic furnaces. This reduction in organic emissions is largely effected by the better mixing and firing characteristics of a liquid or gaseous fuel as compared to those of a solid.

4.9.4 Control Costs

Costs for reducing hydrocarbon emissions from combustion processes are low and may sometimes show an overall profit due to increased combustion efficiency. Switching to another type of fuel may sometimes be more expensive on a cost-per-Btu basis; but when operation, maintenance, and combustion efficiency savings are included, the overall cost may be moderate. In addition, other atmospheric emission problems will be reduced when a more easily burned fuel is used.

Average fuel cost data have been compiled.[43]

4.10 METALLURGICAL COKE PLANTS

4.10.1 Process Descriptions

Coke is mainly produced by the destructive distillation of coal in long rows of narrow rectangular ovens.[43] From 16 to 25 tons of coal is charged through ports in the top of the ovens. The ports are sealed, and the coking period begins because of the intense heat in the oven. In about 16 to 20 hours, when the volatile matter has been driven off and carbonization is complete, the charge is pushed out into quench cars, cooled, and screened.[13] The high-temperature process, during which the coal is heated to temperatures ranging from 1,650° to 2,150°F, is used almost exclusively in the United States.

In the most commonly used by-product ovens, this volatile matter is ducted to equipment that extracts from the gas components such as tar, ammonia liquor, and light oil. Approximately 35 percent of the coke oven gas (heating value, 550 Btu/ft^3) produced during coking is used to heat the coke ovens.[44] Although the remainder of the gas is usually used for heat in other nearby processes, it is sometimes flared.

Coke is also manufactured in beehive-type ovens in which no attempt is made to recover the volatile matter; it is simply vented to the atmosphere. In 1966, only about 2 percent of the total metallurgical coke production of 67.4 million tons was produced in beehive ovens.[45]

4.10.2 Emissions

Visible smoke, hydrocarbons, CO, and other emissions originate from the following by-product coking operations: (1) charging of coal into the red-hot ovens, (2) oven leakage during the coking or carbonization period, (3) pushing the coke out of the ovens, and (4) quenching the hot coke. There are organic emissions, from the last two operations only where the material is undercoked. Although organic compounds are only a part of these emissions, they will also decrease when measures are taken to reduce the more noticeable pollutants.

Soon after an oven has been emptied at the end of the coking cycle, it is refilled with a new charge of pulverized coal. Since the oven interior is at a temperature of 1,500° to 1,800°F, volatilization of gases from the coal mass begins at once. Unless controlled, these gases escape to the atmosphere as visible clouds of yellow-brown smoke.

Because of the nature of the coking process, hydrocarbons and other organic compounds are generated and emitted from the furnaces. Very few quantitative data on organic emissions are available, however.

4.10.3 Control of Emissions[46]

Progress has been made over the years in reducing the quantity of emissions released during the coking process. Improvements in both coke-oven design and operating practices, such as shortening the time required for charging, are responsible for reduced emissions.

One potential improvement over older plants consists of aspirating gases from the interior of the oven by means of steam jet aspirators during charging periods. In older units, the oven interior was sealed off from the gas-collecting duct during charging, and enormous quantities of smoke were emitted. Despite the use of an aspirator during charging, some smoke escapes from openings at the opposite end of the oven because of the distance the gases must travel and because of partial obstruction caused by piling up of coal. One arrangement for minimizing this emission provides two gas-collecting ducts (mains) with a gas ascension pipe and aspirator at each end of the oven. Effective control with this arrangement is greatly dependent on the operators who must regulate the stem valves supplying the jet aspirators.

The use of a leveling bar during the filling operations prevents uneven piling of the coal and assists in keeping the gas-collecting ducts unobstructed.

Emission control systems mounted on the larry car itself have been installed. These systems collect, ignite, and wash the escaping oven gases during the charging process.[47]

The development of volumetric sleeves on the top of the larry car hoppers has made it possible to adjust the bulk of coal in each hopper to match the requirements of ovens of different capacity. This makes it possible to charge the correct volume of coal and thereby minimizes resistance to the passage of gas over the coke within the oven.

Appropriate spacing of the charging holes in relation to oven volume also reduces emissions during charging. Proper spacing eliminates piling up of coal in the oven in such a manner as to obstruct free passage of gases to the gas takeoff flue. In addition, if the bottom ends of the charging holes are flared outward, more space is provided between the coal and the top of the oven for free passage of gases.

Any arrangements that reduce the time required for transfer of the coal charge from the larry car hopper to the oven interior will also reduce the total escape of smoke and organics. Several mechanical devices for this purpose are available, including (1) hopper vibrating mechanisms used in conjunction with smooth stainless steel liners, (2) cylindrical hoppers and bottom turn-table feeders, and (3) a screw-feed mechanism.

Another device, consisting of drop sleeves and shear gates, provides an enclosure between the hopper of the larry car and the top of the charging hole to prevent the escape of gases from the charging hole.

Control of the bulk density of the coal mass is one of the factors contributing to coal feed rate. In coke plants where the coal is pulverized and blended, it has become increasingly common to control the moisture content and, by the addition of small quantities of oil to the coal, to modify the bulk density further. Oil-sprayed coal moves out of the larry car hoppers more easily and can thus be charged faster.

Operation of the steam jet aspirator in the ascension pipe of the oven being serviced is not entirely successful in preventing the escape of smoke. Each oven, however, can be equipped with a smoke seal box, which surrounds the leveling bar opening. In conjunction with the effect of the steam jet aspirator, the seal box greatly reduces the escape of gas from the opening.

The by-product recovery system, which receives the fumes from the gas collecting main, is largely an enclosed process consisting of scrubbers, separators, and distillation columns. The organic compounds shown in Table 4–6 are removed from the coke-oven gas, and the remaining stripped gas is used as fuel. Organic emission may occur from the recovery process because of leaking equipment, pump seals, valve seals, vents, storage tanks, and other relatively minor sources.

Table 4–6. TYPICAL COMPOSITION AND AMOUNTS OF COMPOUNDS REMOVED FROM COKE-OVEN GAS PER TON OF COAL[48]

Compound	Amount, gallons
Benzene	1.85
Toluene	0.45
Xylene and light solvent naphtha	0.30
Acid washing losses	0.16
Heavy hydrocarbons and naphthalene	0.24
Wash oil	0.20

During the carbonization period, leakage may also occur around the oven doors. In older ovens, the joint between the door and the jamb was sealed by luting, that is, by hand-troweling a wet mixture of clay and coke breeze into a channel between the doors and the jamb. Newer oven designs feature self-sealing doors in which metal-to-metal contact between a machined surface and knife edge together with mechanical arrangements for exerting pressure provide the seal. A superior maintenance program must be applied to this equipment since damage to the seal inevitably allows leaks to develop. An optimum maintenance program for self-sealing doors, proposed by coke-oven operators in Allegheny County, Pennsylvania, includes use of stainless steel as the knife-edge material and adoption of systems for (1) keeping a complete history of each door and (2) informing the maintenance force of the reason that a particular door has been taken out of service.

For luted doors, the luting should be tamped immediately after charging is completed in order to prevent emissions.

The quantity of smoke arising from the coke during transportation to the quenching station is dependent on the degree of coking.

Adequately carbonized coke will not smoke when exposed to the air; however, poorly carbonized coke will emit some smoke and hydrocarbons during the short trip to the quenching tower.

The measures discussed above can do much to minimize emissions from coking operations, but no combination of these measures provides a completely satisfactory control method for coke-oven emissions. A satisfactory solution to the problem of emissions during charging has not been developed.[49]

4.11 SEWAGE TREATMENT

4.11.1 Introduction

Municipal sewage is generally treated in a primary treatment plant, an activated-sludge plant, or a trickling filter plant. All of the treatment plants emit organic gases, many of which are odorous. Quantitative data on the nature or amount of emissions, however, are generally lacking and difficult to obtain because sewage treatment plants are essentially outside operations.

Hydrocarbon emissions vary widely from plant to plant, depending on the type of plant and treatment process, the condition and composition of the influent, and the size of the plant.

4.11.2 Process Description and Emissions

A primary sewage treatment plant basically removes only solid material through sedimentation or screening processes. Hydrocarbon emissions therefore only occur from the screening and grit chamber, and from the settling tank itself.

The activated-sludge treatment plant is probably the largest emitter of hydrocarbons when compared with the other two processes.

In the activated-sludge plant, the sewage, after passing through screens and a primary clarifier (settling tank), is aerated with compressed air. Additional sludge, now biologically activated by the air, is settled out in a final clarifier and recycled to the aeration chamber.[50] Various volatile oils, fats, and other organic compounds present in the sewage are partially stripped from the liquid.

Table 4-7 shows the organic vapor concentrations measured in the ambient air above the various treating units at a single activated-sludge plant.

Table 4–7. ORGANIC VAPOR CONCENTRATIONS EMITTED FROM AN ACTIVATED-SLUDGE PLANT[51]

Process	Concentration, μg/liter
Bar screen	35.2
Aeration tank	20
Final clarifier	6.7

In a trickling filter plant, the primary treatment plant is followed by the trickling filter and a final clarifier. The trickling filter is a large bed of coarse, impervious material over which the sewage is sprayed. The sewage trickles down through the bed and comes into contact with the ambient air, which promotes bacterial action.[50] Odors and other organic materials are emitted from the clarifiers and the filter itself.

Sludge collected in the clarifiers is frequently digested in order to render it more innocuous. Sludge digestion generates a methane-rich gas, which may contain trace amounts of hydrocarbons and other odorous material. Digestor gas contains approximately 75 percent methane, 20 percent carbon dioxide, and a balance of oxygen, nitrogen, and trace contaminants. Since the gas has a heating value of about 670 Btu per cubic foot, it is frequently burned in a boiler or in an internal combustion engine at the plant.[50] Direct venting or improper combustion of this gas will result in organic emissions.

4.11.3 Control Techniques and Costs

The basic hydrocarbon and odor control techniques at any sewage treatment plant consist of adequate and careful plant design, proper operation, and diligent maintenance of the treating equipment. Proper plant design calls for the reduction of odor and hydrocarbon emission by eliminating the emission source. Hydrocarbon emissions arising from septic sewage can be reduced by pretreatment with an oxidizing agent such as a chlorate. Frequent cleaning of screens and grit chambers, and preventing the buildup of sludge on walls also reduces organic emissions.

The covering of various treating units such as settling tanks, aeration chambers, and trickling filters and the oxidizing or combusting of effluent gases also serve to reduce emissions.[52] At the Owl's Head Plant in New York City, the gases drawn from the covered settling tanks are treated with ozone to reduce organic emissions and odors. At Mamaroneck, New York, gases vented from the bar screens, grit removal unit, and settling chamber are all treated with ozone.[53] A Sarasota, Florida, plant utilizes a plastic cover over its trickling filter to minimize emissions.[52] Sludge drying beds could also be covered, and the air drawn over the beds for drying could be incinerated before it is released.

Adequate organic emission control involves additional plant construction costs to provide covers for the various processing units. In addition, air blowers, ozone generators, or other gas-oxidizing systems must be installed.

Oxidation ponds are also used to dispose of sewage in some rural areas. These ponds or lagoons are simply holding areas where the natural oxidation processes through surface contact with the air achieve biological breakdown of the sewage. These ponds may emit odorous compounds such as mercaptans and amines, but the main organic gas emitted is methane. This gas is emitted at a rate of about 5 cubic feet per pound of BOD destroyed under a pond loading condition of 55 pounds of BOD per acre per day.[34]

4.12 WASTE INCINERATION AND OTHER BURNING

4.12.1 Introduction

Preliminary results of a survey conducted by the Public Health Service indicate that household, commercial, and industrial solid waste production in the United States is about 10 pounds per capita per day, or 360 million tons per year. About 190 million tons per year (or 5.3 pounds per day per capita) is collected for disposal, and the remainder is either disposed of on site or handled by the household or establishment itself.[55]

An estimated 177 million tons of this material is burned in the open or in incinerators.[56] An additional 550 million tons of agricultural waste and 1.1 billion tons of mineral wastes are generated each year.[55] It is estimated that half of the agricultural wastes are burned in the open. Except for the estimated 48 million tons of coal refuse consumed by fire each year, no other mineral wastes are burned.[56] The quantity of material consumed by forest burning and structural fires is estimated to total about 220 million and 8 million tons a year, respectively.[56]

Incineration and open burning are used to reduce the weight and volume of solid waste. High-temperature incineration with excess air reduces emissions of particulates; carbon monoxide; and smog-forming compounds such as aldehydes, hydrocarbons, and organic acids, which typify open burning. Nitrogen oxides emissions, however, increase.

Figures 4–15 through 4–21 show various basic types of incinerators. In a multiple-chamber design as illustrated in Figure 4–17, combustion products are formed by contact between underfire air and waste on the grates in the primary chamber. Additional air (overfire air) is admitted above the burning waste to promote gas phase combustion. Gases from the primary chamber flow to a small mixing chamber where more air is admitted and then to a larger secondary chamber where more complete oxidation occurs. At times, auxiliary burners are installed in the mixing chamber to increase combustion temperature to about 1,400° to 1,800°F. A total of 150 percent excess air is sometimes supplied to promote oxidation of combustibles. Sizes and configurations of incinerators vary with the service for which they are designed. References 7 and 57 contain information on design parameters for incinerators.

4.12.2 Emissions

Hydrocarbon emissions from incineration and other burning are estimated as shown in Table 4–8.

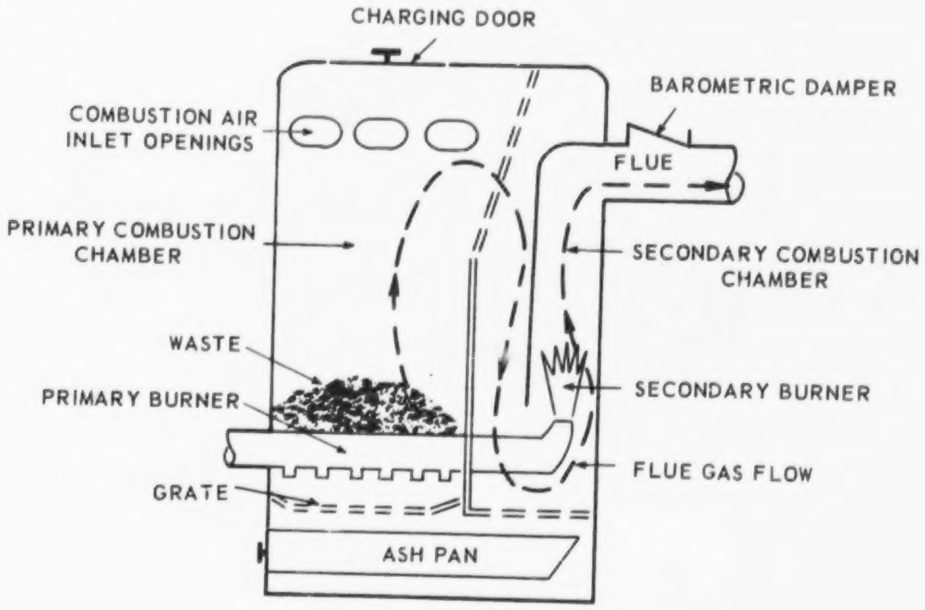
CHARGING DOOR
COMBUSTION AIR INLET OPENINGS
BAROMETRIC DAMPER
FLUE
PRIMARY COMBUSTION CHAMBER
SECONDARY COMBUSTION CHAMBER
WASTE
PRIMARY BURNER
SECONDARY BURNER
FLUE GAS FLOW
GRATE
ASH PAN

Figure 4-15. Domestic gas-fired incinerator.

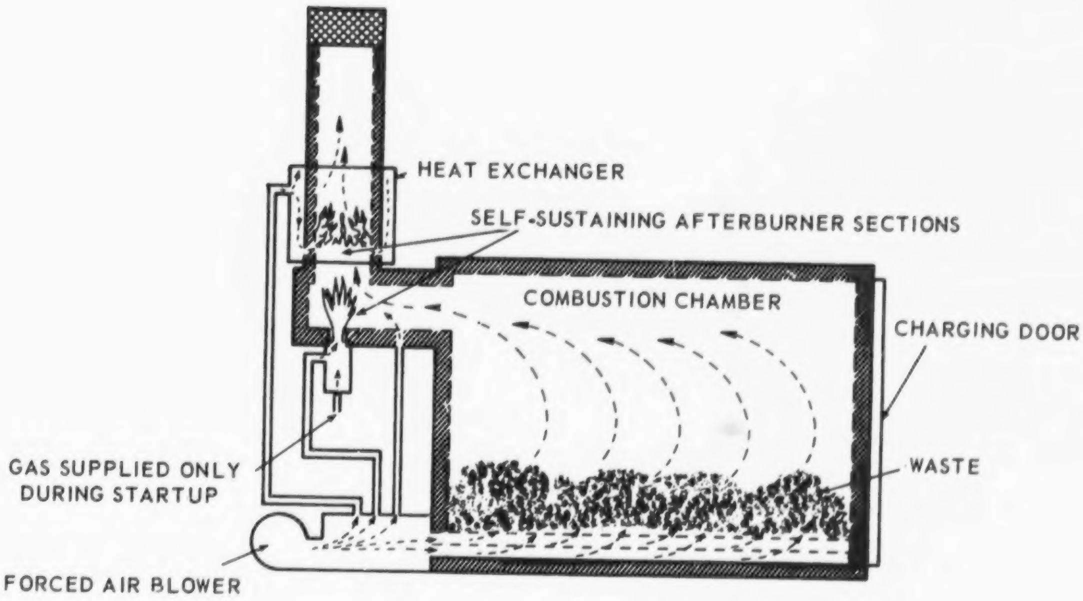
HEAT EXCHANGER
SELF-SUSTAINING AFTERBURNER SECTIONS
COMBUSTION CHAMBER
CHARGING DOOR
GAS SUPPLIED ONLY DURING STARTUP
WASTE
FORCED AIR BLOWER

Figure 4-16. Single-chamber incinerator.

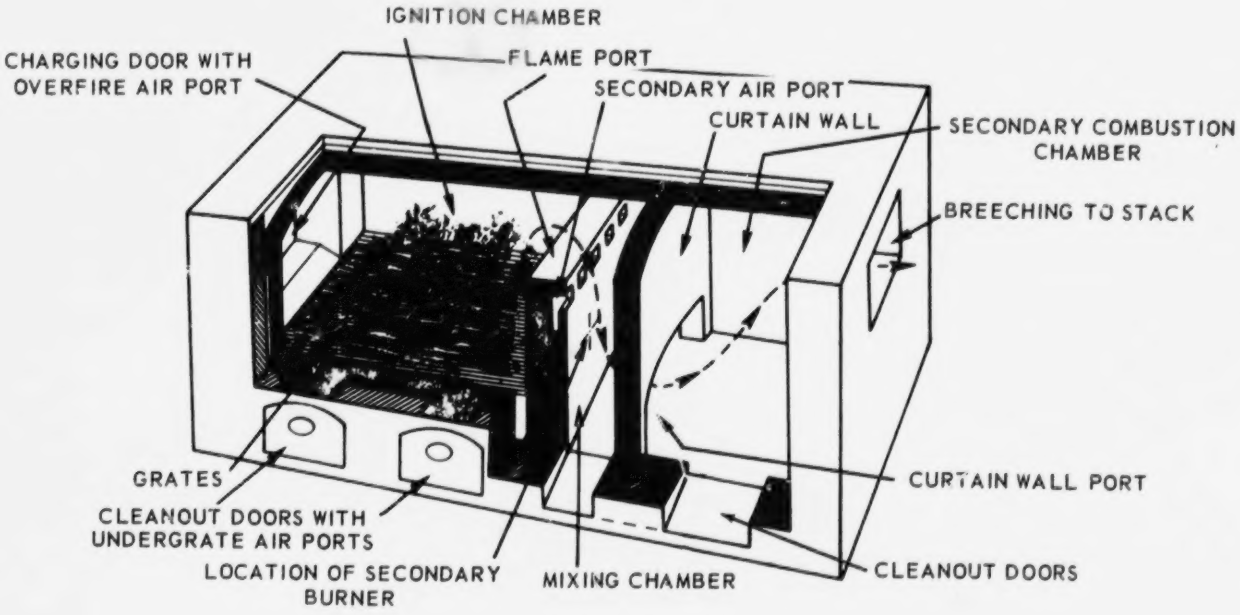
IGNITION CHAMBER
CHARGING DOOR WITH OVERFIRE AIR PORT
FLAME PORT
SECONDARY AIR PORT
CURTAIN WALL
SECONDARY COMBUSTION CHAMBER
BREECHING TO STACK
GRATES
CLEANOUT DOORS WITH UNDERGRATE AIR PORTS
LOCATION OF SECONDARY BURNER
MIXING CHAMBER
CURTAIN WALL PORT
CLEANOUT DOORS

Figure 4-17. Cutaway of an in-line multiple-chamber incinerator.

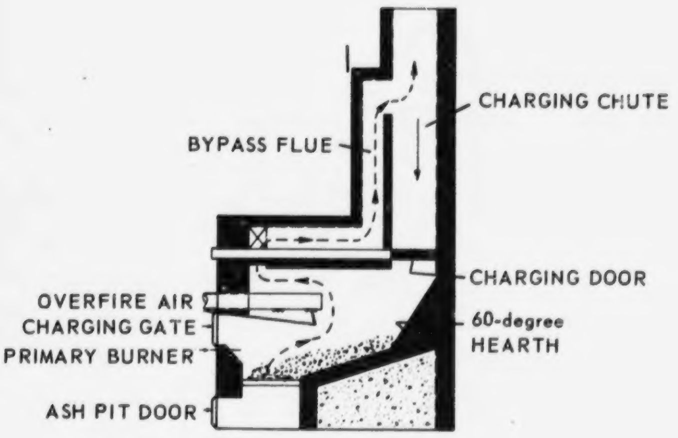
BYPASS FLUE
CHARGING CHUTE
CHARGING DOOR
OVERFIRE AIR
CHARGING GATE
PRIMARY BURNER
60-degree HEARTH
ASH PIT DOOR

Figure 4-18. Section of the flue-fed incinerator.

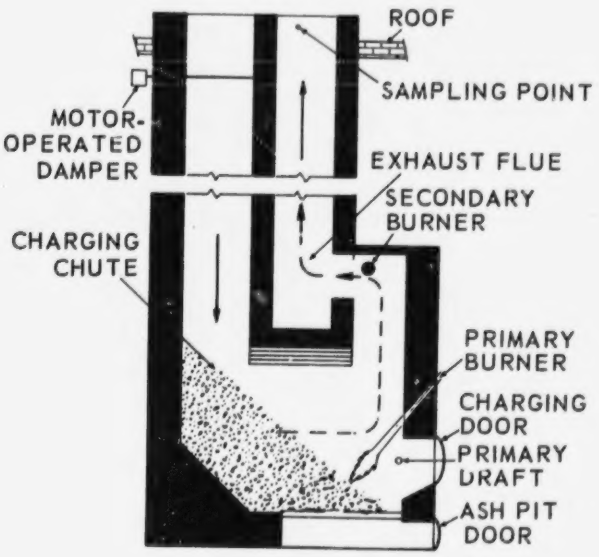
ROOF
SAMPLING POINT
MOTOR-OPERATED DAMPER
EXHAUST FLUE
SECONDARY BURNER
CHARGING CHUTE
PRIMARY BURNER
CHARGING DOOR
PRIMARY DRAFT
ASH PIT DOOR

Figure 4-19. Section of chute-fed apartment incinerator.

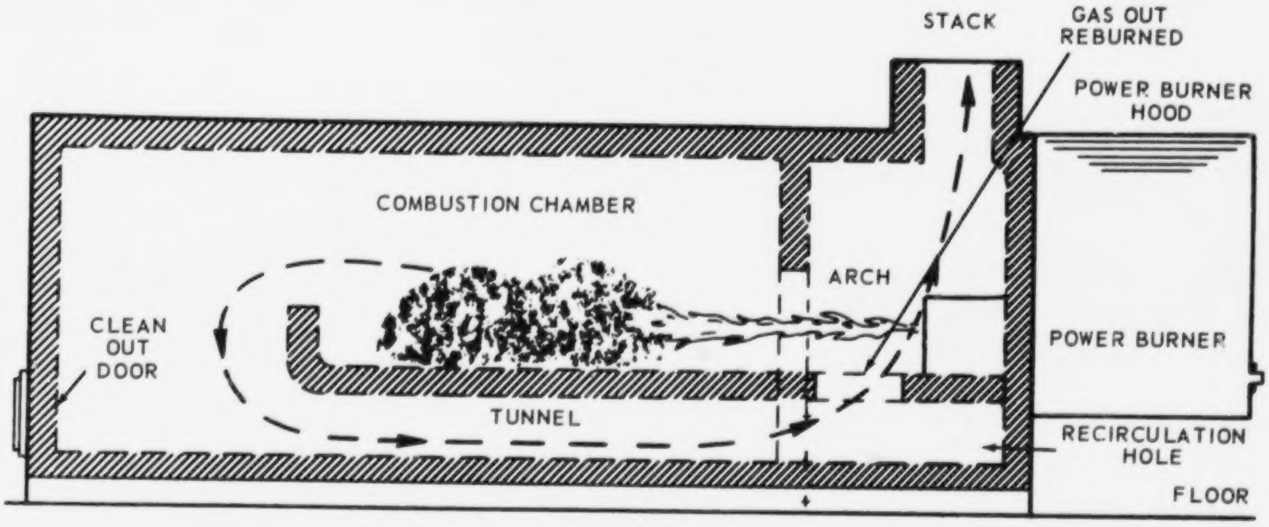
STACK
GAS OUT
REBURNED
POWER BURNER
HOOD
COMBUSTION CHAMBER
ARCH
CLEAN
OUT
DOOR
POWER BURNER
TUNNEL
RECIRCULATION
HOLE
FLOOR

Figure 4-20. Section of pathological incinerator.
(Courtesy of Silent Glow Oil Burner Corp.)

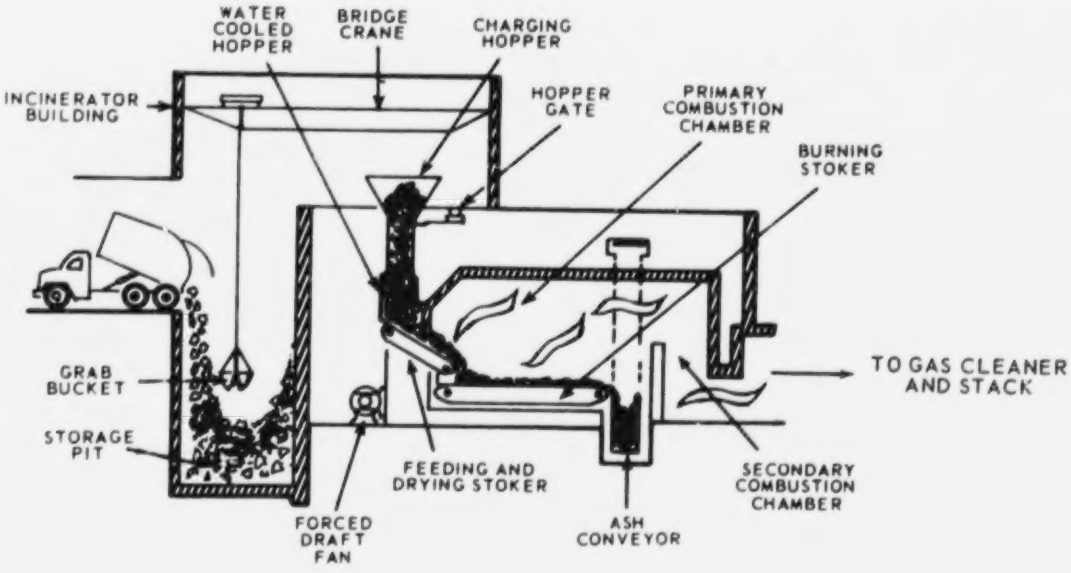
WATER
COOLED
HOPPER
BRIDGE
CRANE
CHARGING
HOPPER
INCINERATOR
BUILDING
HOPPER
GATE
PRIMARY
COMBUSTION
CHAMBER
BURNING
STOKER
TO GAS CLEANER
AND STACK
GRAB
BUCKET
STORAGE
PIT
FEEDING AND
DRYING STOKER
FORCED
DRAFT
FAN
ASH
CONVEYOR
SECONDARY
COMBUSTION
CHAMBER

Figure 4-21. Section of municipal incinerator.

Table 4–8. ESTIMATED NATIONAL EMISSIONS FROM INCINERATION AND OTHER BURNING, 1968[57]

	Quantity, tons/yr	Hydrocarbon emissions, tons/yr
Onsite incineration	57,000,000	29,000
Municipal incineration	16,000,000	2,000
Conical burner incineration	27,000,000	150,000
Open burning	77,000,000	1,150,000
Agricultural burning	275,000,000	1,650,000
Controlled forest burning	76,000,000	760,000
Forest wildfires	146,000,000	1,460,000
Structural fires	8,000,000	80,000
Coal refuse fires	48,000,000	240,000
Total	730,000,000	5,521,000

4.12.3 Controls

High temperature-excess air incineration and substitution of noncombustion alternative waste dispositions are the most likely means for reducing hydrocarbon emissions. Some of these methods are discussed below.

4.12.3.1 Waste Disposal

From the standpoint of air pollution, burning is not a satisfactory method of waste disposal. The sanitary landfill is a good alternative if land for this purpose is available. Approximately 1 acre-foot of land is required per 1,000 persons per year of operation when waste production is 4.5 pounds per day per capita.[58] In addition, soil approximating 20 percent by volume of the compacted waste is required. At times, unavailability of soil limits the use of sanitary landfill.

Unusual local factors may lead to solution of the landfill site problem. Reference 59 indicates that a project is under way in which the refuse is shredded and baled for loading onto rail cars for shipment to abandoned strip-mine landfill sites.

Other alternatives may have application in some localities. Composting has been considered and is being tested on a practical scale.[60] Dumping at sea has been practiced by some seacoast cities, but some of the garbage floats and returns to shore unless dumped far out at sea. Such practices are now forbidden by the United States Government. The Japanese have ground and compressed refuse into bales,[61] which are wrapped in chicken wire and coated with asphalt. The high-density bales sink to the bottom in the deeper ocean areas and reportedly remain intact. The practice of grinding garbage in kitchen units and flushing down the sewer has been increasing. This in turn increases the load of sewage disposal plants and the amount of sewage sludge.

4.12.3.2 Incineration

Although no exact criteria are set for temperature, excess air, or residence time for incinerators, incineration temperatures greater than 1,600°F, more than 150 percent excess air, and heat release rates less than 1,800 Btu per hour per cubic foot of total combustion space are sometimes used as design parameters for hydrocarbon emission reduction. When these conditions are achieved, hydrocarbon emission rates are less than 0.3 pound per ton of waste incinerated.[62]

Where the most effective hydrocarbon emission control is desired, auxiliary burners are used to increase incineration temperature to 1,600°-1,800°F. At temperatures above 1,800°F, slagging of refractories is often a problem. Even when dry combustible wastes are incinerated, auxiliary burners are useful for preheating the secondary combustion sections of the incinerator before the waste is ignited. Temperature control systems promote consistent emission reduction. These are usually on-off-type controls for smaller units and modulating-type controls for larger incinerators.

Incineration air may be supplied by natural or mechanical draft. Recommended stack or chimney dimensions, barometric damper dimensions, and induced-draft fan capacities for various incinerators, air flow, and wastes are published by the Incinerator Institute of America.[63] For the most effective control, air is passed through the grates (underfire air), admitted over the burning waste (overfire air), and admitted in chambers where auxiliary burners are located (secondary air). The ratios between these air supplies vary, depending upon the design of the incinerator. For small incinerators, combustion air is regulated by manual adjustment of air ports at the various points of entry. For larger incinerators, admission of air is regulated automatically, and at times the ratio between air supply at various points is controlled automatically. For 150 percent excess air, the oxygen content of the undiluted gases at the incinerator outlet ranges between 12 and 14 percent, depending upon the type of waste incinerated and the type of auxiliary fuel used.

Sufficient residence time for oxidation of combustibles is provided by furnishing insulated combustion space. A maximum waste and auxiliary fuel heat release of 18,000 Btu per hour for each cubic foot of total combustion space is sometimes used as a design parameter for determining required combustion space. Contact between combustibles in the gas phase and air is promoted (1) by providing baffles, bridge walls, checkerwork, curtain walls, down passes, drop arches, and mixing chambers; (2) by introducing air at strategic locations; and (3) by locating auxiliary burners to promote mixing.

Differences between hydrocarbon emissions from various types of incinerators are caused by differences in incineration conditions. Although insufficient air, combustion space, and mixing increase emission rates, the most common cause of increased hydrocarbon emission rates is low incineration temperature. Estimates of emission rates from various types of incinerators are given in Section 5.

Another way of reducing total hydrocarbon emissions from incineration and combustion is to recover heat in a boiler. That heat would eliminate the need for combustion of some fossil fuels. This means of refuse disposal has already received considerable attention in Europe.[64-68]

In 1966, two 50,000 pound-per-hour steam generators were installed at the Navy Public Works Center in Norfolk, Virginia.[69] They were designed to burn 180 tons of mixed refuse per day in each of two furnaces. The heating value of the mixed refuse is estimated at 5,000 Btu per pound with a 25 percent moisture content and 12.5 percent noncombustibles. Steam is generated from the combustion of the refuse. The waste firing is supplemented by oil firing as required. The furnace walls are water-cooled and integral with the boiler, which reportedly increases steam production by 38 percent.

4.12.3.3 Forest Wildfires

About 1.5 million tons of hydrocarbons is emitted annually from uncontrolled forest fires.[56] These fires are caused by natural elements such as lightning or by careless practices. Considerable activity has been and is being directed toward reducing the frequency of occurrence and the severity of these fires. These activities include publishing and advertising information on fire prevention and control, surveillance of forest areas where fires are likely to occur, and various fire-fighting and control activities. Information on forest fire prevention and control is available from the United States Department of Interior, and state and local agencies.

4.12.3.4 Controlled Vegetation Burning

Forest debris, crop residue, scrub, brush, weeds, grass, and other vegetation are burned for one or more of the following purposes:

1. To control vegetation, insects, or organisms harmful to plant life.
2. To reduce the volume of waste.
3. To minimize fire hazards.
4. To improve land.

Hydrocarbon emissions from this burning are estimated to be 2.4 million tons per year.[56]

Collection and incineration of these wastes in properly controlled incinerators would reduce emission rates from an estimated 12 to 20 pounds per ton to less than 0.3 pound per ton.[56]

Other alternatives to incineration are abandonment or burying at the site, transport and disposal in remote areas, and utilization. Abandonment or burying at the site is practical in cases where no harmful effects will ensue. Because abandoned or buried vegetation can have harmful effects upon plant life, such as hosting harmful insects or organisms, agricultural agencies such as the U.S. Department of Agriculture or state and local agencies should be consulted before these techniques are employed. Other harmful aspects such as odor, potential water pollution, and fire hazards should also be considered. Collection and transport of these materials for disposal in areas where the effects of burning will cause no problem is possible, but not commonly practiced.

At times it is possible to use some of these waste materials. Large forest scraps are processed by chipping or crushing and used as raw materials for kraft pulp mills or processes producing fiberboard, charcoal briquettes, or synthetic firewood. Composting and animal feeding are other possible alternatives to burning.[60]

4.12.3.5 Coal Refuse Fires

An estimated 240,000 tons of hydrocarbons is emitted each year from 19 billion cubic feet of burning coal refuse.[57] Extinguishing and preventing these fires are the techniques used for eliminating emissions from them. These techniques involve cooling and repiling the refuse, sealing refuse with impervious material, injecting slurries of noncombustibles into the refuse, minimizing the quantity of combustibles in the refuse, and preventing ignition of the refuse. These techniques and the status of future plans and research are described and discussed in the document *Control Techniques for Sulfur Oxide Air Pollutants.*[70]

4.12.3.6 Structural Fires

Structural fires emit an estimated 80,000 tons of hydrocarbons annually.[56] Prevention and control techniques are used to reduce these emissions. Use of fireproof construction, proper handling, storage, and packaging of flammable materials and information programs on fire prevention are some of the techniques used to prevent fires. Fire control techniques include the various methods for promptly extinguishing fires such as the use of sprinklers, foam, and inert gas systems; provision of adequate fire fighting facilities and personnel; and provision of adequate alarm systems. Information on these and other techniques for fire prevention and control are available from agencies such as insurance companies, local fire departments, National Fire Protection Association, and the National Safety Council.

4.12.4 Costs

The cost of controls is primarily a function of the relative costs of the various methods of incineration and the cost of noncombustion disposition. As cost comparisons vary widely from locality to locality, comparisons should be made on an individualized basis. Information that may be useful for guiding cost comparisons is presented below.

According to a recent survey, the average community budgets $5.39 per capita per year for waste collection. Communities operating their own facilities budget about $6.80 per capita per year for twice-a-week collection and about $5.60 per capita per year for once-a-week collection.[55] Sanitary landfill costs including amortization have been reported as $1.05 per ton for 27,000 tons per year of waste and $1.27 per ton for 11,000 tons per year.[55] Figure 4-22 shows average operating costs for sanitary landfill and open-dump waste-disposal methods.[55]

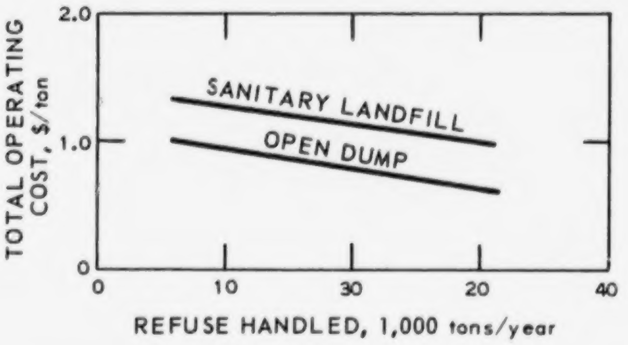

Figure 4-22. Land waste-disposal costs.[56]

Operating costs for municipal incinerators are estimated at $4 to $8 per ton of waste, and capital costs are estimated at from $6,000 to $13,000 per ton per day capacity. Estimated capital costs of incinerators are shown in Figure 4-23.

Auxiliary fuel requirements for increasing the incineration temperature to 1,600°F with 150 percent excess air vary from zero for dry combustible waste to an estimated 15,000 Btu per pound for wastes containing 75 percent moisture and having a heating value of 3,500 Btu per pound.

4.13 MISCELLANEOUS

4.13.1 Introduction

Almost any processing of organic matter results in the emission of hydrocarbons. Such diverse activities as chocolate manufacturing, bread baking, pharmaceutical manufacturing, leather tanning, coffee roasting, food processing, fermentation, tobacco aging, and charcoal manufacture all result in the emission of some organic compound. The following processes illustrate the sources and nature of hydrocarbon emissions. Quantitative emission information is not generally available.

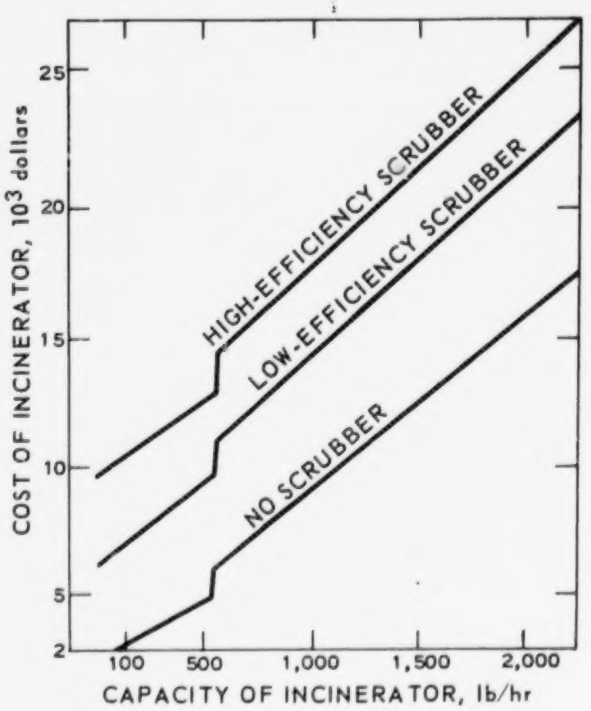

Figure 4-23. Cost of incinerator at three levels of control of particulate emissions.[73]

4.13.2 Fermentation Processes

The manufacture of beer, wine, whiskey, and other fermented beverages results in the emission of organic compounds, largely alcohols. These emissions come from distilling operations, cooking or brewing kettles, vacuum systems, fermenters, and aging or storage processes. Air pollution controls for organic emissions, other than condensers, which are an integral part of the process, are not used. In the manufacture of distilled liquors (whiskey, gin, etc.), one of the larger sources of organic emissions is the aging warehouse where the liquor is kept for 1 to 5 years in wooden barrels. During this time, evaporation occurs through the barrel staves.[12] The drying of the "slop" or still bottoms, which are used for animal feed, also results in organic emissions. This drying is accomplished in either rotary or vacuum drum driers.

4.13.3 Food Processing

Many food processing operations emit organic compounds. Deep fat frying (French frying) of various baked goods, vegetables, fish, and meat results in the vaporization of various oils in the material being fried. Excessive heating of the cooking oil vaporizes some of the oil itself.[7] Objectionable organic emissions from these processes are best controlled by afterburners.

Coffee roasting also releases odorous organic compounds, which derive from the volatile matter present in the green coffee beans. Because of the relatively high boiling point of many of these compounds (saturated and unsaturated fats, furfural compounds, etc.), they tend to condense after leaving the roaster and form particulate matter. Control of organic and smoke emissions may be accomplished by venting part of the exit gases back through the roaster, or by installing an afterburner.[73,74]

The canning of fish and other perishable foods results in organic emissions from the oils and fats present in the food. The canning of fish is probably most objectionable because of the malodorous organic compounds emitted. Fish may be either precooked before canning (usually confined to large fishes like tuna) or canned and cooked before sealing (sardines, anchovies, etc.). After the cans are sealed, they are pressure-cooked. Condensed steam, oils, and juices collected during the cooking processes are collected for by-product recovery. In addition to the collected oils and juices, the inedible parts of fish are also processed into by-products such as fish meal, high-protein concentrates, and fish solubles. This reduction of the inedibles produces the major organic odorous emissions in the form of trimethylamine, $(CH_3)_3N$.

Many types of equipment are employed to control gases at a fish canning and reduction plant. These devices include condensers on the cooking processers, condensers and afterburners on the evaporators, and afterburners or chlorinated water scrubbers on the fish meal drier gases.[12]

4.13.4 Charcoal Manufacture

The destructive distillation of wood to produce charcoal, wood alcohol, and acetic acid is accomplished by heating hard wood in an enclosed retort. Approximately 44 pounds of methane and other noncondensible organic compounds is emitted for each cord of wood (4,000 lb).[12] Since this gas also contains about 27 percent carbon monoxide, and has a heating value of 150 to 250 Btu per cubic foot, it is usually burned as fuel at the plant. Combustion of this wood gas effectively controls the hydrocarbon emissions.

4.13.5 Drug Manufacture

Drugs and pharmaceuticals encompass a broad spectrum of materials, ranging from purified anesthetic-grade ethers and other anesthetics to the extraction and purification of cod-liver oil. "Biological" odors are conventionally controlled by incineration. Solvents may be recovered by adsorption. Pill coating, with chocolate or other taste-controlling materials, can emit odors that are not unpleasant, but are annoying if persistent. Incineration and adsorption are the most effective means of control. Usually there is no provision for recovery of the adsorbed materials. Frequently, the use of packaged replaceable adsorption units is feasible.

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5. EMISSION FACTORS

For an accurate air pollution survey, whether for a single source or for a metropolitan area, pollutant emissions must be identified by type and quantity.

Ideally, in order to determine emission rates, a stack analysis of all sources of possible emission would be necessary; but this is impossible, of course, when an air pollution survey must cover a large area, which could contain several thousand sources. Emissions from sources that have not been measured and analyzed must, therefore, be estimated. Estimates are determined by the use of *emission factors*, which are pollutant emission rates based on stack-sampling data, material balances, and engineering appraisals of the same type of sources.

Because emission factors may at times be based on limited or variable data, emission factors should be used with caution unless the data upon which the factor is based have been studied or reviewed.

Table 5-1 is a compilation of available emission factors for hydrocarbons from various types of sources. These emissions rates are for uncontrolled sources unless otherwise noted. Except where noted, emission factors were compiled from a Public Health Service publication.[1] For some cases in which a range of emission factors is given, the range reflects the figures given by different sources.

Table 5–1. EMISSION FACTORS FOR HYDROCARBONS

Source	Hydrocarbon emissions, lb/unit given	Unit
Fuel combustion–stationary sources		
Coal combustion unit		
$<10 \times 10^6$ Btu/hr capacity	10	ton of coal
10 to 100 x 10^6 Btu/hr capacity	1	ton of coal
Greater than 100 x 10^6 Btu/hr capacity	0.2	ton of coal
Fuel Oil		
$<10 \times 10^6$ Btu/hr capacity	3	1,000 gal of oil
10 to 100 x 10^6 Btu/hr capacity	2	1,000 gal of oil
Greater than 100 x 10^6 Btu/hr capacity	0.8	1,000 gal of oil[a]
Solid waste disposal		
Open burning on site of leaves, brush, paper, etc.	12	ton of waste
Open burning dump	30	ton of waste
Municipal incinerator	0.3	ton of waste
Multiple-chamber incinerator	0.5	ton of waste
Single-chamber incinerator	0.8	ton of waste
Flue-fed incinerator	2	ton of waste
Domestic incinerator		
No control	2	ton of waste
Afterburner	1	ton of waste

Table 5–1 (continued). EMISSION FACTORS FOR HYDROCARBONS

Source	Hydrocarbon emissions, lb/unit given	Unit
Process industries		
Phthalic anhydride plant		
Oxidation of napthalene vapors with excess air over catalyst	32	ton of product
Petroleum refinery (as total hydrocarbons)		
Boilers and process heaters	140	1,000 bbl oil
Fluid catalytic unit	220	1,000 bbl fresh feed
Moving-bed catalytic cracking unit	87	1,000 bbl fresh feed
Compressor internal combustion engines	1.2	1,000 ft^3 fuel gas
Blowdown system		
With control	5	1,000 bbl refinery capacity
Without control	300	1,000 bbl refinery capacity
Process drains		
With control	8	1,000 bbl waste water
Without control	210	1,000 bbl waste water
Vacuum jets		
With control	Negligible	1,000 bbl vacuum distillation capacity
Without control	130	1,000 bbl vacuum distillation capacity
Cooling towers	6	10^6 gal cooling water capacity
Pipeline valves and flanges	28	1,000 bbl refinery capacity
Vessel relief valves	11	1,000 bbl refinery capacity
Pump seals	17	1,000 bbl refinery capacity
Compressor seals	5	1,000 bbl refinery capacity
Air blowing, blend changing, and sampling	10	1,000 bbl refinery capacity
Storage		
V.P.$\geq$1.5 psia-fixed roof	47	1,000 bbl refinery capacity
V.P.$\geq$1.5 psia-floating roof	4.8	1,000 bbl storage capacity
V.P.<1.5 psia-fixed roof[b]	1.6	1,000 bbl storage capacity
Commercial operations		
Dry cleaning		
Chlor-hydrocarbons	1.7	per capita per year
Hydrocarbon vapors	2.2	per capita per year
Gasoline handling (evaporation)		
Filling tank vehicles		
Splash filling	8.2	1,000 gal throughput
Submerge filling	4.9	1,000 gal throughput
Filling service station tanks		
Splash filling	11.5	1,000 gal throughput
Submerge filling	7.3	1,000 gal throughput
Filling automobile tanks	11.6	1,000 gal throughput

[a] From reference 2.

[b] From reference 3.

Examples of how emission factors are used are given below:

1. Coal combustion:
   Given: Power plant burns 100,000 tons per year of coal in a steam generator of 450×10^6 Btu/hr capacity.
   Find: Annual hydrocarbon emissions.

$$(100{,}000 \text{ tons/yr.}) \left(0.2 \frac{\text{lb HC}}{\text{ton of coal}}\right) = 20{,}000 \text{ lb of HC/yr.}$$

2. Petroleum refinery, fluid catalytic cracking unit:
   Given: Fluid catalytic cracking unit with 10,000 barrels per day of fresh feed; operates 350 days per year and has no CO boiler.
   Find: Annual hydrocarbon emissions.

$$(10{,}000 \text{ barrels/day}) \left(\frac{220 \text{ lb HC}}{1{,}000 \text{ bbl}}\right) (350 \text{ day/year})$$

$$= 770{,}000 \text{ lb of HC/year.}$$

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6. ECONOMICS

6.1 INTRODUCTION

Economic considerations in air pollution control include: (1) definition of alternatives, (2) identification of costs, (3) cost curves by equipment types, (4) value of recovered materials, (5) selection of control systems, and (6) assessment of economic impact. Each of these if discussed below.

6.2 DEFINITION OF ALTERNATIVES

The process of selecting a control system should be begun by identifying the total control needs of a plant. Usually more than one problem exists, and attacking pollution problems together is more economical than trying to handle each one separately. The advantages and disadvantages of the substitution of fuels or raw materials, and the modification or even replacement of the processes can best be assessed with the total needs in view, since these methods tend to reduce or eliminate more than one problem. Such methods also tend to have an effect on solid waste disposal and water pollution problems. If process alterations or substitutions are not feasible, then effluent control equipment is necessary. In most cases, the problems can be remedied in several ways. The economic analysis of the different ways is an approach to the selection of one of them for a given problem. Other considerations are the effects that the emissions may have on the company's relations with the public and the growth potential for the plant or process.

An important factor in making the choice among control equipment alternatives is the degree of reduction of emissions required to meet emission standards. The degree of emission reduction or collection efficiency required depends upon the reduction required before the level of emission falls below the level permitted. The usual ranges of collection efficiency for various types of control equipment are discussed in Section 3.

Factors to be considered next are the process stream characteristics. flow rate, temperature, moisture content, explosiveness, particle content, odor, corrosiveness, and ignition point. For consideration of afterburners, the quantity of auxiliary fuel must be determined. The temperature modifications (heat transfer) necessary if adsorption is to be applied must be defined. The conditions for absorption must be determined. Power requirements for pumps, compressors, or blowers must be estimated. Space required for the control system is often an important consideration.

Plant facilities should be planned to include equipment for waste treatment, product recovery, and heat recovery.

Each alternative that meets all requirements can then be evaluated in terms of cost.

6.3 IDENTIFICATION OF COSTS

Cost estimates, useful in comparing alternative control systems, are best developed using techniques available for preliminary capital cost estimating. An excellent source of such a method, together with equipment cost relationships, is the "Capital Cost Estimating" procedure, published in *Chemical Engineering* on March 24, 1969.[1]

The definable control costs are those that are directly associated with the installation and operation of control systems. These expenditures have a breakdown for accounting purposes as follows:

1. Capital investment

   Engineering studies, design costs, land, structural modification, construction overhead, dismantlement, rearrangement, lost production, control hardware, auxiliary equipment, installation, and startup.

2. Maintenance and operation

   Utilities, labor, supplies and materials, treatment and disposal of collected material, supervision, plant overhead, and employee benefits.

3. Capital charges

   Taxes, insurance, interest, and depreciation.

Some of these expenditures vary from place to place and are therefore not discussed further. Typical costs are engineering studies, land acquisition, structural modifications, and operating supply inventory. The others are discussed as a group.

6.3.1 Capital Investment

The "installed costs," often quoted by manufacturers on the basis of their engineering studies, include control hardware, auxiliary equipment, and installation costs. These costs vary with the rate of exhaust to be treated and with the collection efficiency of the control device. Installed costs include a reasonable increment for erection, insulation material, transportation of equipment, site preparation, clarifiers and liquid treatment systems, and auxiliary items such as fans, ductwork, motors, and control instrumentation.

According to a recent survey conducted by the American Institute of Plant Engineers, installation added an average of 49.7 percent to the cost of control equipment.[2] The lowest average installation cost, 16 percent of equipment price, was in the aerospace industry. The highest, 81 percent, was in the chemical industry.

6.3.2 Maintenance and Operation

Maintenance cost is the expenditure required to sustain the operation of control devices at their designed efficiency with a scheduled maintenance program and necessary replacement parts. The costs of operation and maintenance depend upon the quality and suitability of the control equipment, the user's understanding of its operation, and his vigilance in maintaining it. Maintenance labor takes an average of 16 percent of a plant's control budget, and spare parts and materials account for 10 percent.[2]

Annual operating cost is the expense of operating a control device at its designed collection efficiency. This cost depends upon the gas volume cleaned, the pressure drop across the system, the operating time, the electricity consumed, the mechanical efficiency of the fan, the scrubbing liquor consumed, and axuliary fuel used. About 43 percent of a pollution control operating budget is spent for power, fuel, and water; collected waste disposal accounts for 31 percent.[2]

6.3.3 Annualized Costs

Annualized capital costs are estimated by depreciating the capital investment (total installed cost) over the expected life of the control equipment, and adding the capital charges (taxes, interest, and insurance). Adding the recurring maintenance and operation costs to this figure gives the total annualized cost of control. Operation costs include disposal of collected materials, if this operation incurs added costs. In some cases these materials will have value. The control system sometimes adds value to the primary products by improving their quality.

Certain simplifying assumptions allow the annualized cost to be estimated, if more specific information pertinent to a given case is not available.[3] These assumptions are as follows:

1. Purchase and installation costs are depreciated over 15 years, a period assumed to be a reasonable economic life for control devices.
2. The straight-line method of depreciation (6-2/3 percent per year) is the easiest to use in cost formulas since it has the simplicity of a constant annual writeoff.
3. Other capital costs–interest, property taxes, insurance, and miscellaneous–are assumed to be equal to the amount of depreciation, 6-2/3 percent of the initial capital cost of the control equipment installed. Thus depreciation plus these other annual charges

amount to 13-1/3 percent of the initial capital cost of the equipment.

4. Electric power costs reflect electricity used by all systems directly associated with the control equipment, and are computed on the marginal rate classes on a constant usage basis at a specified gas volume.
5. The user of control equipment is assumed to establish a scheduled preventive maintenance program designed to maintain equipment at its optimum collection efficiency. Unscheduled maintenance, such as replacement of defective parts, is undertaken as required.

Some business firms use an interest rate to compute capital costs as in item 3 above only when money is actually borrowed. When capital is supplied from company assets, the "cost of capital" is the before-tax earnings, which could be obtained by investing the capital in some other opportunity.[4] This is frequently called the "opportunity cost of capital" and varies widely by industries and individual firms. It is usually higher than the cost of borrowed capital.

6.4 COST CURVES BY EQUIPMENT TYPES

For the convenience of those who may use the cost information described in this section, a series of control equipment cost curves are provided (Figures 6-1 through 6-4). These curves represent costs in a normal situation. If the installation requires special measures in site preparation, supporting structures, utility installations, or if other unusual costs are incurred, the total cost of the control installation can be substantially higher than indicated by these curves.

6.4.1 Afterburners

For control of particulates, puchase costs have been correlated with afterburner capacity using data from the literature, from personal experiences, and from questioning users, installers, and suppliers of pollution control equipment.[3] Assuming no basic change in costs for afterburners to control organic liquids and vapors, the "purchase cost" curve in Figure 6-1 may be used to estimate equipment costs from the volume-flow rate of the gas to be treated. The curve may be updated by means of the Chemical Engineering Plant Cost Index. Costs of heat exchangers do not appear in the curve and are therefore an extra cost item if used.

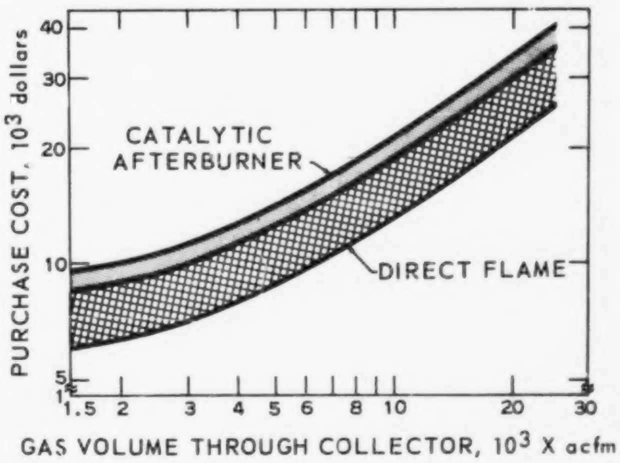

Figure 6-1. Purchase cost of afterburners, 1968.

Given the equipment-cost estimate, the other cost components can be estimated by suitable relation thereto. Depending upon local conditions, installation costs range from 10 to 50 percent of the equipment costs, and, rarely, as high as 100 percent. Annual maintenance costs run approximately 6¢ per cubic foot per minute (cfm) and 20¢ per cfm for catalytic afterburners.

6.4.2 Activated-Carbon Adsorbers

Adsorption systems have been installed, in many cases, to recover a valuable component economically. Economic return depends on the amount of material that can be recovered. Where organic vapors exist at very low concentrations, the value of the recovered material may be sufficient to cover operating costs only if the recovery unit is relatively large. The value of recovered material weighed against investment and operating costs determines the least expensive method of removing organic vapors whether the system pays for itself or not.

Figure 6-2 shows the installed-cost estimates of adsorbers versus the flow rate of the stream to be treated. Based on the results of pilot plant experiments by Elliot[5] et al., in which vapors from protective coating operations were treated, these costs include superheater, condenser, decanter, blower, blower motor, cooling tower, water pump, filters, filter housing, initial carbon charge, carbon vessel and screens, and ducts. The installation costs were set equal to the total cost of all equipment; therefore, the installed costs shown are twice the equipment costs.

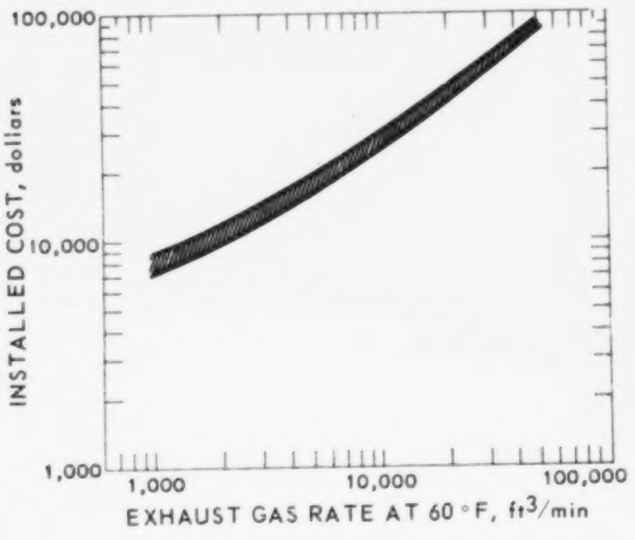

Figure 6-2. Adsorption system installed costs, 1969 basis.

Installed cost estimates are $6.80 to $8.00 per cfm for a 1000-cfm system. For 50,000-cfm systems, the cost ranges from $1.54 to $1.70 per cfm.[5] The estimates for the higher ranges are based on extrapolation of pilot plant data. Since no units of these sizes have been built, the projections are conjectural.

Operating cost estimates have been reported by Mantell[6] and by Barnebey and Davis.[7] According to Mantell, the recovery expense for typical activated-carbon systems, operating with a solvent vapor concentration of 30 to 50 percent of the lower explosive limit, may be less than 0.2¢ per pound of solvent recovered and seldom more than 1¢ per pound, based on the 1951 economy. Barnebey and Davis report operating costs up to 4¢ a gallon without distillation of the recovered product (1959). Neither author included maintenance expense in arriving at operating costs.

6.4.3 Absorption Equipment

The cost of absorption equipment can only be estimated by an engineering study of each particular problem, since, as has been shown, the nature of the component to be absorbed determines the materials of construction and the kind of packing.[8] It is recommended that each case be referred to professional engineers and vendors of control equipment for actual cost quotations.

For a first estimate of the primary costs of a packed tower, however, Figure 6-3 may be used together with an estimate of the tower height required, as discussed in Section 3.4.5. This figure shows the installed cost per foot of height of packed tower versus the flow rate of gas to be treated.

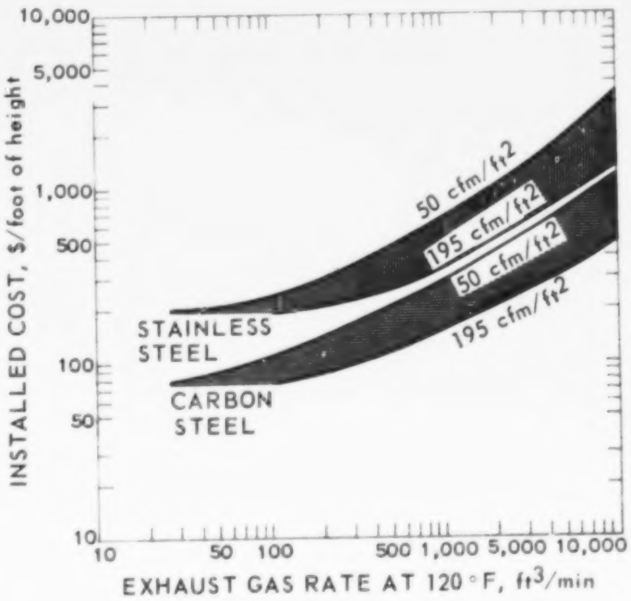

Figure 6-3. Packed tower costs, with Raschig rings as packing, 1969 basis.[9]

Costs are shown for carbon steel and for stainless steel. Raschig rings were assumed to be the packing material. For these, gas flow rates can range from 50 to 150 cubic feet per minute per square foot (air at 80°F). These limits are shown in the figure.

6.4.4 Condensers

The basic costs for both contact-type and surface condensers (shell and tube) are shown in Figure 6-4. The data for these curves were obtained from the reference given on each curve. The cost of surface condensers is based on the critical factor in sizing these units, namely, the heat transfer area. The cost of contact-type condensers is based on the average gas volume through the unit. Both types of condensers are available as package units and thus require a minimum of field labor for installation.

Operating costs for condensers are not excessive. Pressure drop of the vapor passing through these units is on the order of 1 inch of water. Costs of water consumed, pumping, disposal, and, in some cases, operation of a cooling tower must be included in the annual operating charge.

6.5 VALUE OF RECOVERED MATERIALS

Numerous industrial plants throughout the country are proving that the pollution problem can be solved and that the recovered materials are worth more than their recovery costs. Whether the recovered materials will pay for the cost of control depends largely upon the size of the operation and the value of the particular materials.

Pollution abatement systems can result in recovery of raw materials and energy or the production of saleable by-products. The value of these items should be utilized in an economic analysis by estimating their dollar

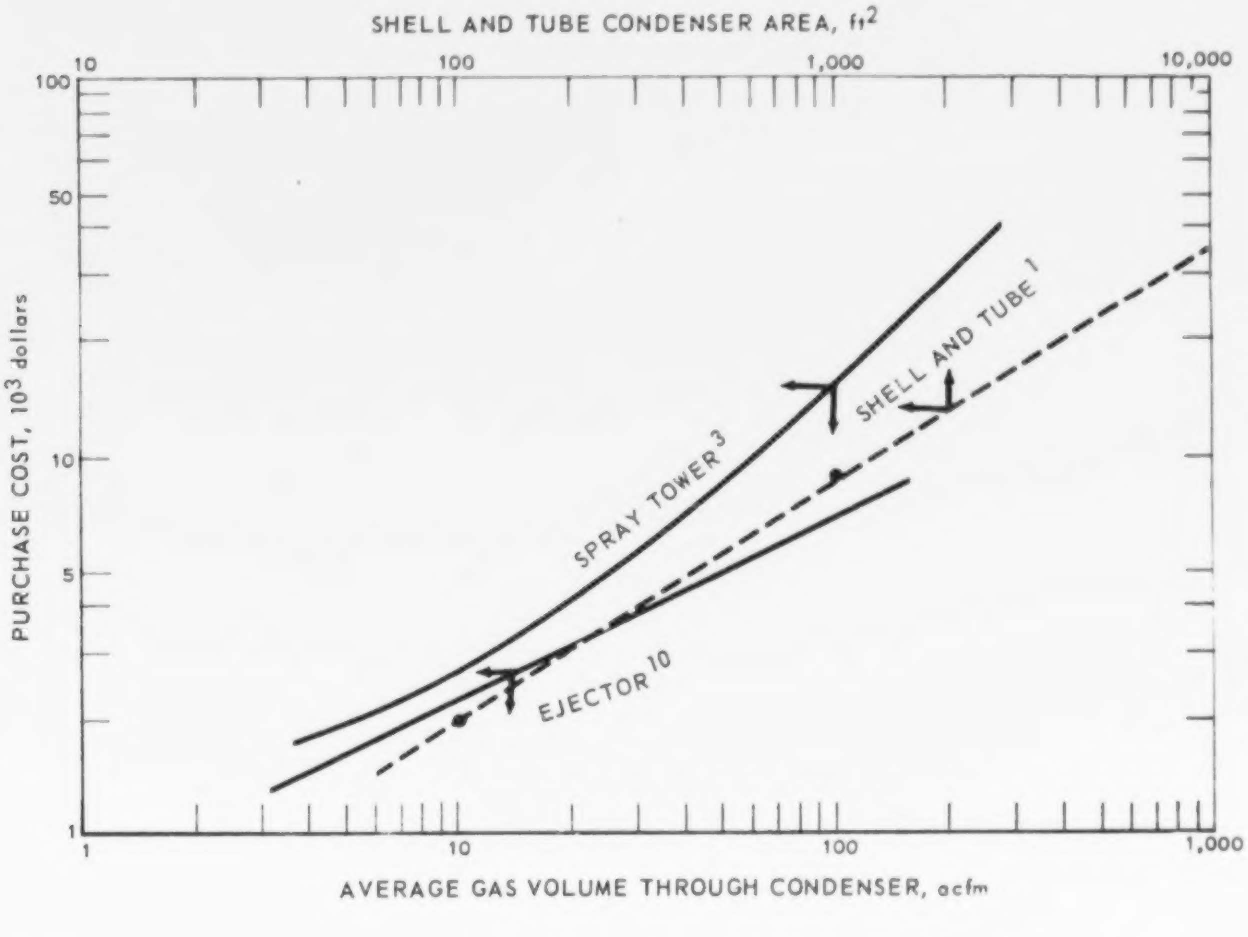

Figure 6-4. Purchase costs of condensers.[1, 3, 10]

values and applying the values as credits to the annualized cost of the systems under study. In some cases the control system increases the value of the primary products by improving their quality.

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7. CURRENT RESEARCH

7.1 RESEARCH PROJECTS APPLICABLE TO HYDROCARBONS AND ORGANICS

A summary of 800 air pollution research projects active during Fiscal Year 1967 is given in reference 1. All projects that were applicable to hydrocarbons and organics from stationary sources are listed in Section 7.3. The projects are listed in alphabetical order by the reference 2 code number and are categorized according to various subject areas. The control equipment and techniques section is divided into various subheadings such as absorption, adsorption, incineration, scrubbing, halogenation, catalysis, and pyrolysis.

The increase in research on air pollution can be seen by comparing the approximately 800 research projects active during Fiscal Year 1967 with the 501 projects active during Calendar Year 1966. A summary of the 1966 air pollution research can be found in reference 3. This report shows that 22 percent of the total funding was applied to control devices or methods, 13 percent was applied to source and source emission studies, and 16 percent was applied to health effects.

7.2 RESEARCH ON CONTROL EQUIPMENT AND TECHNIQUES

There is a continuing effort to improve equipment for controlling hydrocarbons and organics. In addition to research being sponsored by the industries that create air pollutants, the companies that make the equipment are continuously striving to improve their product or are trying to develop new and better control techniques.

One study sponsored by the National Air Pollution Control Administration during 1967-1968 was a $212,230 contract to Pope, Evans, and Robbins to study fluidized-bed combustion.[4]

One major part of industrial air pollution results from exhausting large volumes of air that are contaminated with organic vapors at concentrations too small to recover economically. A process called the Zorbcin Process is said to purify the air to the extent that it can be recycled back into the plant air. This could give the added benefit of reducing large heating and air-conditioning loads in process plants that require frequent air changes.

The Zorbcin Process consists of forcing plant exhaust air through one or more activated-carbon beds to remove the organic contaminant. The purified air is either discharged to the atmosphere or returned to the plant area. When the carbon bed becomes saturated with organics, it is removed from the adsorption cycle and regenerated by circulating hot air through the bed. Regenerating air flow is appreciably lower than contaminated air flow to each adsorber. A slip stream from the regenerating air is sent to an air incinerator or a catalytic combustion chamber where the stripped organic vapor is burned. The slip stream is less than one-tenth of the contaminated air flow. A small amount of natural gas is burned in the incinerator to insure complete combustion of the organics and to supply any additional heat required for carbon regeneration. Direct mixing or heat exchange transfer this heat to the regenerating air.

At the end of the regenerating cycle, the remaining regenerating gas is purged and exhausted either to the atmosphere or into the contaminated air stream. Since the regenerating air and exhaust from the incinerator are ultimately cleaned by passing through an activated adsorber, complete combustion in the incinerator is not required to guarantee high-purity air leaving the system.

The system is adaptable to moving-bed or fixed-bed adsorption systems. Also since the vapors are held above their dew point, no corrosive condensate will be involved. Thus inexpensive construction materials can be used.

The developers of the Zorbcin Process state that some development work is still needed before an optimum commercial unit can be delivered. Desorption characteristics data for various organic vapors at different concentrations and regenerating air temperatures are lacking.

A new platinum catalyst has been designed especially for air pollution problems.[2] This catalyst was originally developed for nitric acid tail-gas decolorization, but has proved effective for the elimination of hydrocarbon and organic vapor contaminants.

The new family of ceramic catalysts are in the form of a honeycomblike structure. The advantages of these honeycomb catalysts are stated to be:

1. A much lower pressure drop (for a gas flow of 10 scfm per square inch of catalyst bed, the pressure drop through the honeycomb was 1 inch of water per inch of bed depth and compared with 24 inches of water through a standard pellet bed of 1/8-inch pellets).
2. A more uniform gas distribution.
3. A greater structural strength.
4. No attrition or loss of fines.
5. No channeling or hot spots.

When tested on various hydrocarbons and organics, the ceramic catalysts were found to be effective for completely oxidizing N-heptane and other solvents such as xylene, methyl ethyl ketone, acetone, and alcohols.

In absorption research, a new method of increasing interfacial area for gas-liquid contacting in cocurrent flow employs screen packings.[5] Interfacial area was found to be increased twofold to fourfold by the presence of a screen packing. Liquid-phase mass transfer coefficient was found to be virtually independent of gas flow, but dependent on liquid flow rate.

7.3 CURRENT RESEARCH PROJECTS

This section is a summary of current air pollution research projects that apply to hydrocarbons and other organics from stationary sources. This following list, compiled from reference 1, includes both foreign and domestic projects, and the reference codes given in alphabetical order were taken directly from it. The first six letters of the code are the first six letters of the last name of the principal investigator. The two digits in the middle of the code indicate the organization supporting the research and may be obtained from reference 1. The projects were categorized by subject and include all projects active or begun during the Fiscal Year 1968. If information on the location and address of the organization conducting the research is desired, the reader is referred to reference 1.

Reference Code	Subject
	Combustion
Battig -50-SLA	Safe Limits of Air Pollution From Products of Fuel Combustion
Crietz -09-CP	Combustion Products
Grumer -11-FCC	Flame Characteristics Causing Air Pollution
Grumer -13-FCC	Flame Characteristics Causing Air Pollution
Hangeb -11-CER	Combustion Emission Reduction
Long -10-RHD	Reduction of Hydrocarbons During Incomplete Combustion
Newhal -10-CPA	Combustion Process Analysis
Parris -18-APG	Air Pollution-Generating Stations
Powers -17-APE	Aerodynamic Properties of Engine Exhaust Plumes
Powers -17-APE	The Aerodynamic Properties of Engine Exhaust Plumes
Robiso -11-CCA	Characterization and Control of Air Pollutants

	From a Fluidized Bed Combustion Unit
Starkm -10-CGC	Combustion Gas Composition
Tebben -10-ABC	Aromatic By-Products of Combustion
Unknow -11-AEO	Atmospheric Emissions from Oil-Fired Power Plants Control Equipment and Techniques
Engel -96-CGA	Cycled Gas Absorption
Low -10-FAC	Fundamentals of Air Cleaning by Sorption Processes
Moore -10-SAP	Study of Air Pollutants by Absorption Spectroscopy
Saffer -72-DAC	Development of Activated Carbon for Air Conditioners
Shulma -10-KAM	Kinetics of Adsorption by Molecular Sieves
Zwiebe -10-MEA	Multicomponent Equilibrium Adsorption - Air Pollution
Satter -10-HCA	Hetero-Homogeneous Catalysis of Air Pollutants
Cote -11-GGP	Guide to Good Practice for Flue Fed Incinerators
Dorsey -11-MIC	Municipal Incinerator Control Development
Essenh -10-IPE	Incineration Processes and Emissions
Gitsen -53-IOS	Incineration of Organic Sludge
Kaiser -10-CIM	Continuous Incineration of Municipal Refuse
Kaiser -10-SIB	Smokeless Incineration of Bulky Refuse
Sables -11-GGP	Guide to Good Practice for Direct-Fed Multiple Chamber Incinerators
Seifer -10-IWT	Incinerator Water Treatment System and Air Pollution Scrubber Test
Smith -10-DII	Demonstration of Improved Incinerator Technology for a Small Community
Stengl -51-MI	Municipal Incinerator
Unknow -11-AEM	Atmospheric Emission from Municipal Incinerators
Waid -64-FIA	Fume Incineration Applications
Kaiser -10-PMR	Pyrolisis of Municipal Refuse Industrial processes and hydrocarbon sources
Chandl -05-CFF	The Contribution of Forest Fires to Atmospheric Pollution
Krotch -11-CSD	Cooperative Study to Develop Control Devices
Margol -11-NPR	New Process Research
Neal -10-ACD	Atmospheric Carcinogens in a Dense Petro-Chemical Area
Ozolin -11-MIP	Major Industry and Process Emission Surveys
Ryan -09-FSP	Field Studies Planned Fires
Unknow -11-AEP	Atmospheric Emissions from Petroleum Refineries

7.4 REFERENCES FOR SECTION 7

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SUBJECT INDEX

A

Absorbents
  selection criteria, 3-14
Absorbers
  types of, 3-14–3-16
Absorption
  applications of, 3-14
  costs of equipment, 6-4–6-5
  principles of operation, 3-16–3-19
  selection of absorbents, 3-14
  types of absorbers, 3-14–3-16
Adsorbents
  types of, 3-9
Adsorbers
  cost of, 6-3
  factors in the selection of, 3-12–3-13
Adsorption
  applications of, 3-8–3-9
  basic operating principles, 3-7–3-8
  control of the process, 3-13–3-14
  description of the process, 3-9
  selection of an adsorber, 3-12–3-13
  types of adsorbents, 3-9
Afterburners
  basic operating principles, 3-2–3-5
  criteria for selection of, 3-6–3-7
  costs of, 6-3
Air-blowing of asphalt
  in petroleum refining, 4-7–4-8

C

Catalytic afterburners, 3-3–3-5
Charcoal manufacture, 4-46
Chemical plants
  collection of vented gases, 4-17
  disposal of waste gases, 4-18
  halogenation, 4-17–4-18
Chemical treating system, 4-8
Coal refuse fires, 4-44

Condensation
  basic operating principles and equipment, 3-21
  condenser design factors, 3-21–3-23
  general discussion of, 3-19–3-21

Condensers
  costs of, 6-5
  design factors and applications, 3-21–3-23
  operating principle, 3-21
  types of, 3-21

Control systems (industrial processes)
  chemical plants, 4-16–4-18
  degreasing operations, 4-30–4-31
  dry cleaning, 4-32–4-33
  gasoline distribution systems, 4-8–4-13
  lacquer manufacture, 4-18–4-21
  metallurgical coke plants, 4-35–4-37
  paint manufacture, 4-18–4-20
  petroleum refineries, 4-1–4-8
  rubber and plastic products manufacture, 4-25–4-26
  sewage treatment, 4-37–4-38
  stationary fuel combustion, 4-33–4-34
  surface coating application, 4-27–4-28
  varnish manufacture, 4-23–4-25
  waste incineration and other burning, 4-42–4-45

Costs
  annualized costs, 6-2–6-3
  capital investments, 6-2
  control system alternatives, 6-1
  degreasing operations, 4-30–4-31
  dry cleaning, 4-32–4-33
  equipment cost curves, 6-3–6-5
  gasoline distribution systems, 4-13
  maintenance and operation costs, 6-2
  sewage treatment, 4-37–4-38
  stationary fuel combustion, 4-34
  surface coating applications, 4-27–4-28
  waste incineration, 4-44–4-45

Cracking catalyst regeneration
  in petroleum refineries, 4-6

D

Degreasing operations, 4-28–4-31
Direct flame afterburners, 3-2–3-3
Drug manufacture, 4-46
Dry cleaning, 4-31–4-33

E

Economics
  of pollution control, 6-1–6-6
Emission factors, 5-1–5-3
Emissions
  charcoal manufacture, 4-46
  chemical plants, 4-13–4-16
  degreasing operations, 4-28–4-30
  drug manufacture, 4-46
  dry cleaning, 4-32
  fermentation processes, 4-45
  food processing, 4-45–4-46
  gasoline distribution systems, 4-9–4-10
  metallurgical coke plants, 4-35
  paint, lacquer, and varnish manufacture, 4-18–4-22
  petroleum refineries, 4-1–4-8
  rubber and plastic products manufacture, 4-25–4-26
  sewage treatment, 4-37
  stationary fuel combustion, 4-33
  surface coating applications, 4-27
  waste incineration, 4-38–4-42

F

Fermentation processes, 4-45
Food processing, 4-45–4-46
Forest wildfires, 4-43–4-44
Fuel substitution
  control of stationary fuel combustion, 4-34

G

Gasoline distribution systems
  bottom loading, 4-11–4-12
  controls, 4-10–4-12
  costs, 4-13
  emissions, 4-9–4-10
  overhead loading, 4-10–4-11
  regulations and costs, 4-13
  vapor disposal, 4-12

H

Hydrocarbon emission sources, 2-1–2-2

I

Incineration
  basic operating principles and equipment, 3-1–3-6
  selection of an afterburner, 3-6–3-7
  waste disposal, 4-42–4-43

L

Lacquer manufacturing, 4-20–4-21
Los Angeles County
  rule 66, 3-24–3-26

M

Metallurgical coke plants, 4-34–4-37

O

Oil-water effluent systems, 4-5–4-6
Operating principles and equipment
  absorption, 3-16–3-19
  adsorption, 3-7–3-8
  catalytic after burners, 3-3–3-5
  condensation, 3-21
  direct flame afterburners, 3-2–3-3
  process heaters and boilers, 3-6
  stationary fuel combustion, 4-33–4-34

P

Paint, lacquer, and varnish manufacture, 4-18–4-25
Paint manufacturing, 4-18–4-20
Petroleum refinery emission sources
  air-blowing of asphalt, 4-7–4-8
  boilers and process heaters, 4-8
  chemical treating processes, 4-8
  cracking catalyst regeneration, 4-6
  flares, 4-5
  general discussion, 4-1–4-3
  loading facilities, 4-8
  oil-water effluent systems, 4-5–4-6
  pressure relief systems, 4-4
  pumps, 4-6–4-7
  storage, 4-3–4-4
  vacuum jets, 4-8
  valves, 4-8
  waste gas disposal systems, 4-4–4-5
Photochemical reactions
  discussion of, 2-1
Photochemical reactivity
  of trichloroethylene, 3-26
  regulation 3 of San Francisco Bay Area, 3-26
  regulations based on reactivities, 3-24–3-26
  rule 66 of Los Angeles County, 3-24–3-26
  use of in controlling organic emissions, 3-23–3-26
Plastics manufacture (*See* Rubber and plastics products manufacture)
Process heaters and boilers, 3-6
Pumps
  petroleum refineries, 4-6–4-7

R

Recovery
  of raw materials, 6-5–6-6
Regulation 3
  San Francisco Bay Area, 3-26
Research, 7-1–7-3
Rubber and plastic products manufacture, 4-25–4-26
Rule 66 of Los Angeles County
  background of, 3-24–3-26
  provisions of, 3-24

S

San Francisco Bay Area Control District
  regulation 3, 3-26
Sewage treatment, 4-37–4-38
Sources
  hydrocarbon emissions general discussion, 2-1–2-2
  organic solvent emissions general discussion, 2-1–2-2
Stationary fuel combustion, 4-33–4-34
Storage emissions, 4-3–4-4
Surface coating operations, 4-26–4-28
  costs, 4-27–4-28

T

Trichloroethylene
  photochemical reactivity of, 3-26

V

Vapor degreasing equipment, 4-30–4-31
Varnish manufacturing, 4-21–4-25
Vegetation burning, 4-44

W

Waste-gas disposal systems
  flares, 4-5
  pressure relief systems, 4-4
Waste incineration and other burning, 4-38–4-45